JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

Committee of Publication:

A. Chaston Chapman.
A. W. Crossley, C.M.G., D.Sc., F.R.S.
M. O. Forster, D.Sc., Ph.D., F.R.S.
A. Harden, D.Sc., Ph.D., F.R.S.
T. A. Henry, D.Sc.
C. A. Keane, D.Sc., Ph.D.
G. T. Morgan, D.Sc., F.R.S.
J. C. Philip, O.B.E., D.Sc., Ph.D.
W. J. Pope, C.B.E., M.A., D.Sc., F.R.S.
F. L. Pyman, D.Sc., Ph.D.
A. Scott, M.A., D.Sc., F.R.S.
S. Smiles, O.B.E., D.Sc., F.R.S.
J. F. Thorpe, C.B.E., D.Sc., Ph.D., F.R.S.

Editor:

J. C. Cain, D.Sc.

Sub-Editor:

A. J. Greenaway.

Assistant Sub-Editor:

Clarence Smith, D.Sc.

Abstractors:

G. Barger, M.A., D.Sc.
H. W. Bywaters, D.Sc., Ph.D.
H. M. Dawson, Ph.D., D.Sc.
C. H. Desch, D.Sc., Ph.D.
W. Godden, B.Sc.
E. Goulding, D.Sc.
H. B. Hutchinson, Ph.D.
G. F. Morrell, Ph.D., D.Sc.
T. S. Patterson, D.Sc., Ph.D.
T. H. Pope, B.Sc.
T. Slater Price, D.Sc., Ph.D.
E. H. Rodd, D.Sc.
S. B. Schryver, D.Sc., Ph.D.
W. P. Skertchly.
F. Soddy, M.A., F.R.S.
J. F. Spencer, D.Sc., Ph.D.
L. J. Spencer, M.A.
R. V. Stanford, M.Sc., Ph.D.
D. F. Twiss, D.Sc.
A. Jamieson Walker, Ph.D., B.A.
J. C. Withers, Ph.D.
H. Wren, M.A., D.Sc., Ph.D.

1918. Vol. CXIV. Part I.

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C. 4.
1918.

Abstractors of the *Journal of the Society of Chemical Industry*, who have contributed to this volume.

J. F. Briggs.	J. H. Lane.
T. F. Burton, B.Sc.	C. A. Mitchell.
L. A. Coles.	B. North.
W. F. Frew.	A. B. Searle.
H. J. Hodsman.	A. Shonk.
J. H. Johnston.	F. C. Thompson.
C. A. King.	

Printed in Great Britain by Richard Clay & Sons, Limited
Brunswick St., Stamford St., S.E. 1, and Bungay, Suffolk.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Use of Metal-ammoniums in Organic Chemistry. E. CHABLAY (*Ann. Chim.*, 1917, [ix], **8**, 145—220).—A résumé of work already published (compare A., 1905, i, 502; 1906, i, 722; 1907, i, 53; 1911, i, 939; 1912, i, 3, 244, 528; 1913, i, 438).

W. G.

The Method of Pyrogenic Decomposition of Methyl Alcohol at High Temperatures. (MLLE.) EGLANTINE PEYTRAL (*Compt. rend.*, 1917, **165**, 703—705).—From determinations of the relative amounts of carbon monoxide and formaldehyde obtained when methyl alcohol vapour is passed at different rates through a platinum tube at 1150°, it is shown that the decomposition takes place in two stages which proceed simultaneously. In the first stage, formaldehyde and hydrogen are formed, and the formaldehyde is then decomposed, giving carbon monoxide and hydrogen.

W. G.

A Hydrate of a Salt Precipitated by Warming its Aqueous Solution. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **100**, 355—356).—Barium ethyl phosphate, $BaC_2H_5PO_4$, is prepared by warming together on the water-bath for some hours a mixture of ethyl metaphosphate, $C_2H_5PO_3$, and methyl alcohol, and subsequently neutralising with barium hydroxide. When the aqueous solution of the barium salt is warmed, crystals separate, which re-

dissolve on cooling. The crystals seem to be a hydrated form of barium ethyl phosphate. They can also be precipitated from aqueous solution by means of alcohol. E. H. R.

The Preparation and Hydrolysis of Esters derived from the Substituted Aliphatic Alcohols. W. A. DRUSHEL and G. R. BANCROFT (*Amer. J. Sci.*, 1917, [iv], **44**, 371—380).—A description of experiments on the rate of hydrolysis of the acetates derived from ethyl, β-hydroxyethyl, β-methoxyethyl, α- and β-ethoxyethyl, α- and β-chloroethyl, and β-bromoethyl alcohols by aqueous $N/10$-hydrochloric acid.

β-Hydroxyethyl acetate, b. p. 187—189°, was obtained by digesting equimolecular proportions of ethylene glycol and acetic acid for eight hours over anhydrous copper sulphate (2 mols.); attempts to prepare β-hydroxyethyl acetate by reaction with anhydrous potassium acetate and alcoholic ethylene bromide yielded only glycol diacetate. The β-ethoxyethyl alcohol necessary for the production of the corresponding acetate was formed by digesting equimolecular quantities of β-bromoethyl acetate and sodium ethoxide for half an hour in alcoholic solution.

With a halogen atom or alkyloxy-group attached to the α-carbon atom of an ethyl ester, the rate of hydrolysis is too rapid to be measured in the ordinary way; α-chloroethyl acetate, α-chloroethyl propionate, and α-ethoxyethyl acetate undergo almost instantaneous hydrolysis in $N/10$-hydrochloric acid, yielding the corresponding fatty acid, together with a mixture of acetaldehyde and hydrogen chloride in the first two cases and of acetaldehyde and ethyl alcohol in the case of the third ester.

The β-substituted acetates at 25° to 45° undergo hydrolysis less rapidly than ethyl acetate, the hydroxyl and alkyloxyl groups and the halogens producing approximately the same degree of retardation; the ethoxyl radicle produces a slightly greater effect than the methoxyl radicle, whilst bromine is of somewhat less influence than chlorine. The temperature-coefficients for the β-substituted esters range from 2·2 to 2·5 for 10°, the values of the coefficient for the β-bromoethyl acetate being slightly lower than for the other esters. In the case of the β-substituted esters, the hydrolysis follows a normal course, although the β-halogen compounds at the higher temperatures tend to form small quantities of hydrogen chloride or bromide. D. F. T.

Selenium Dioxide-Oxalic Acid, its Preparation and Theoretical Significance. TH. GASSMANN (*Zeitsch. physiol. Chem.* 1917, **100**, 209—214).—Two grams of selenium dioxide are dissolved in concentrated hydrochloric acid and the solution evaporated almost to dryness on the water-bath. The residue is moistened with dilute hydrochloric acid and then 25 c.c. of a 33% solution of potassium oxalate are added. After mixing, a white, flaky precipitate gradually forms, which is collected and dried. *Selenium dioxide-oxalic acid*, $SeO_2(C_2H_2O_4)_2$, is thus

obtained as a white powder, which turns brown on heating at 90° or exposure to light. The elementary composition of the material is not thereby altered, which suggests that the alteration in colour is due to an intramolecular change. The author considers that in the new compound the four carboxyl radicles are combined directly with the selenium atom, which thereby becomes octavalent, $SeO_2(CO_2H)_4$. It is also suggested that the selenium found in bones and teeth (Gassmann, A., 1916, i, 772) is present in the form of a compound analogous in structure to selenium dioxide-oxalic acid. H. W. B.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. IV. Racemic and Optically Active Complex Salts of Rhodium Trioxalic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 263—279. Compare A., 1915, i, 867; ii, 399; this vol., i, 7).—Complex compounds of the type $[MeX''_3]Y_n$ should, according to Werner's theory, have a molecular structure the configuration of which exhibits asymmetry of the trigonal trapezohedral class. Failure to detect enantiomorphism in the crystals of the optically active substances in triethylenediamine compounds of this type is to be attributed to the chemical identity of the radicles around the central atom. In cases where these radicles contain oxygen, however, the expected hemihedrism is found. The *d*- and *l*-potassium rhodium oxalates, which have now been examined, form right- and left-handed crystals of the expected type of symmetry. Werner's claim to have resolved the racemic compound by spontaneous crystallisation cannot be substantiated. Indeed, from physico-chemical considerations, it is impossible, since the *d*- and *l*-compounds are more soluble than the *r*-salt. Werner's supposed hemihedral crystals were probably distorted trigonal crystals of the racemic compound. The optical rotation of the active compounds is specially interesting, for solutions of the *d*-compound are inactive for light of wave-length 5970 Ångström units, dextrorotatory for smaller, and lævorotatory for greater wave-lengths. At wave-length 5970, the optical antipodes are indistinguishable from the racemic compound. For this wave-length there is no trace of an absorption line, and the idea of a connexion between abnormal rotation dispersion and selective absorption must be given up.

r-Potassium rhodium oxalate, $K_3[Rh(C_2O_4)_3],4\frac{1}{2}H_2O$, garnet-red, transparent plates, triclinic [$a:b:c=1.0732:1:1.0316$; $\alpha=98°10\frac{2}{3}'$; $\beta=104°17\frac{1}{3}'$; $\gamma=66°11\frac{2}{3}'$].

d- and *l*-Potassium rhodium oxalate ($+H_2O$) form blood-red, massive crystals of varying habit belonging to the trigonal trapezohedral class [$a:c=1:0.8938$; $\alpha=100°38'$]. The hemihedral character of the crystals is shown by the occurrence of the trigonal bipyramid $\{22\bar{4}\bar{1}\}$ and $\{2\bar{2}\bar{4}1\}$ on the *d*- and *l*-crystals respectively.

The silver rhodium oxalate, $[Rh(C_2O_4)_3]Ag_3$, has been prepared in long, red needles, and from it, by interchange with triethylene-

diaminerhodium halogenides, nine possible racemic and active isomerides of the complex compound, $[Rh(C_2H_8N_2)_3][Rh(C_2O_4)_3]$.

r-Potassium rhodium malonate, $[Rh(C_3H_2O_4)_3]K_3,3H_2O$, forms orange-red, monoclinic plates [$a:b:c=1\cdot2309:1:1\cdot0783$; $\beta=86°36'$].

r-*Potassium iridium oxalate* ($+4\frac{1}{2}H_2O$) is isomorphous with the corresponding rhodium salt. It forms beautiful, lustrous orange crystals, triclinic [$a:b:c=1\cdot0771:1:1\cdot0405$; $\alpha=98°38\frac{1}{2}'$; $\beta=104°3'$; $\gamma=66°9\frac{1}{2}'$]. E. H. R.

Complex Salts of Ferrimalonic Acid. F. M. JAEGER and R. T. A. MEES (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 283—291).—The strychnine and brucine salts of ferrimalonic acid crystallise in small, greenish-yellow crystals, but after fractionation and elimination of the alkaloid, only optically inactive solutions were obtained. The tristrychnine salt (str = strychnine), $[Fe(C_3H_2O_4)_3]str_3,6H_2O$, showed a rotation corresponding approximately with the alkaloid present, and no active potassium salt was obtained. The ferrioxalates could not be resolved by means of their diammonium-strychnine, -quinine, -cinchonine, or -morphine salts, or by means of the corresponding hydrazine salts. The following *racemic salts have been prepared and examined crystallographically*. There appear to be three series of hydrated salts of the alkali metals, rhombic and triclinic salts with $1H_2O$ and triclinic salts with $4H_2O$.

Potassium ferrimalonate, $K_3[Fe(C_3H_2O_4)_3],4H_2O$, large, transparent, emerald-green triclinic crystals [$a:b:c=0\cdot4924:1:0\cdot4897$; $\alpha=98°5'$; $\beta=104°30'$; $\gamma=82°52\frac{1}{2}'$].

Ammonium ferrimalonate, $(NH_4)_3[Fe(C_3H_2O_4)_3],H_2O$, pale green, dichroic plates, rhombic bipyramidal [$a:b:c=0\cdot9407:1:0\cdot6860$].

Rubidium ferrimalonate, $Rb_3[Fe(C_3H_2O_4)_3],H_2O$, isomorphous with the last [$a:b:c=0\cdot9442:1:0\cdot6985$]. A triclinic monohydrate was also observed, but could not be measured.

Cæsium ferrimalonate, $Cs_3[Fe(C_3H_2O_4)_3],H_2O$, isomorphous with the rhombic rubidium salt [$a:b:c=0\cdot9548:1:0\cdot7089$].

Thallous ferrimalonate, $Tl_3[Fe(C_3H_2O_4)_3],H_2O$, rhombic, well-developed, flat plates, isomorphous with the last [$a:b:c=0\cdot9615:1:0\cdot7050$].

Thallous malonate, $Tl_2C_3H_2O_4$, is very soluble in water, and separates only from highly supersaturated solutions in large, transparent, monoclinic crystals [$a:b:c=0\cdot5707:1:1\cdot0833$; $\beta=81°30\frac{1}{2}'$]. E. H. R.

c

Hyposulphites. X. Diformaldehydesulphoxylic Acid [Hydroxymethyl Hyposulphite]. A. BINZ [with R. HUETER and E. GOLDENZWEIG] (*Ber.*, 1917, **50**, 1274—1286. Compare A., 1915, i, 801).—Sodium formaldehydesulphoxylate (rongalite) reacts with formaldehyde and hydrochloric acid according to the equation $ONa\cdot S\cdot O\cdot CH_2\cdot OH + HCl + CH_2O = S(O\cdot CH_2\cdot OH)_2 + NaCl$. The product, *hydroxymethyl hyposulphite* ("diformaldehydesulphoxylic

acid"; "dihydroxydimethylene sulphoxylate"), can be obtained in the form of comparatively stable solutions, which may be concentrated by evaporation under reduced pressure. Sulphurous acid, on the other hand, only combines with one molecular proportion of formaldehyde, and then only when applied in the form of acid salts (for example, $NaHSO_3$), and the solutions decompose on evaporation. Directions are given for the preparation of 30% solutions from formalin or 79% solutions from methyl-alcoholic formaldehyde.

The new substance reacts with one molecular proportion of potassium hydroxide to give potassium formaldehydesulphoxylate and formaldehyde, thus:

$$S(O{\cdot}CH_2{\cdot}OH)_2 + KOH = OH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}OK + CH_2O + H_2O.$$

It also reacts with four atomic proportions of iodine, according to the equation $S(O{\cdot}CH_2{\cdot}OH)_2 + 4I + 2H_2O = H_2SO_4 + 4HI + 2CH_2O$. This disposes of the sulphone and sulphoxide formulæ, $H{\cdot}SO_2{\cdot}H$ and $H{\cdot}SO{\cdot}OH$, for hyposulphurous acid. Bazlen has shown, however, that formaldehydesulphoxylic acid is dibasic, at any rate in its barium salt, and ascribes to the acid the formula

$$SH(OH)_2{\cdot}O{\cdot}CH_2{\cdot}OH.$$

This corresponds with a hyposulphurous acid of the type $SH(OH)_3$, analogous, therefore, to $H{\cdot}SO{\cdot}OH$. In order to reconcile Bazlen's salt (A., 1905, ii, 240) with the above theories, it is assumed that the alcoholic hydrogen has acidic properties. The salt is therefore represented by $O{<}{\substack{S{-}O \\ CH_2{\cdot}O}}{>}Ba,2H_2O$ rather than by

$$OH{\cdot}CH_2{\cdot}O{\cdot}SH{<}{\substack{O \\ O}}{>}Ba,H_2O.$$

The chief difficulty connected with the formula $S(O{\cdot}CH_2{\cdot}OH)_2$, however, is that one formaldehyde molecule is very easily eliminated, whilst the other remains until the sulphur atom is oxidised to the sexavalent condition. Perhaps it may be possible to account for this on stereochemical grounds, as in Hinsberg's theory (A., 1916, i, 725).

A solution of hydroxymethyl hydroxybenzyl hyposulphite, $OH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}O{\cdot}CHPh{\cdot}OH$, can also be obtained, by mixing rongalite, hydrochloric acid, and benzaldehyde.

If powdered rongalite is warmed with chloromethyl methyl ether, a small yield of *hydroxymethyl methoxymethyl hyposulphite* can be obtained, as a colourless oil, thus: $OH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}ONa + CH_2Cl{\cdot}OMe = OH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}O{\cdot}CH_2{\cdot}OMe + NaCl$.

The hydroxyl groups in the above hyposulphites can be replaced by the residues of primary amines if the esters and bases are mixed in ethereal solutions. Solid products separate as a rule. The following examples are given. Hydroxymethyl hyposulphite and ammonia give *aminomethyl hyposulphite*, $S(O{\cdot}CH_2{\cdot}NH_2)_2$, as a sticky mass; aniline yields *anilinomethyl hyposulphite*, in white leaflets, m. p. 131° (decomp.); methyl anthranilate forms *o-carbomethoxyanilinomethyl hyposulphite*,

$$S(O{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Me)_2,$$

in needles, m. p. 169—171°; *p*-anisidine gives p-*methoxyanilinomethyl hyposulphite*, m. p. 105°; *o*-phenylenediamine yields *o-aminoanilinomethyl hydroxymethyl hyposulphite*,

$$OH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}O{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2,$$

m. p. 116°. From the ethereal solution of hydroxymethyl hydroxybenzyl hyposulphite, the following compounds have been obtained: with *p*-toluidine, p-*toluidinomethyl* α-*hydroxybenzyl hyposulphite*, m. p. 125—126°; with anthranilic acid, o-*carboxyanilinomethyl* α-*hydroxybenzyl hyposulphite*, m. p. 168° (decomp.). The latter ester reacts with potassium cyanide to form o-*carboxyanilinoacetonitrile*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CN$, m. p. 181°.

J. C. W.

Two Crystallised Isomeric Lævulose Penta-acetates. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 280—282).—The two penta-acetates were prepared from a lævulose tetra-acetate, the α-form by means of zinc chloride and acetic anhydride, the β-form by strong sulphuric acid and acetic anhydride (A., 1915, i, 502).

α-Lævulose penta-acetate crystallises from a mixture of alcohol and chloroform in rhombic, bisphenoidal prisms [$a:b:c = 0.4946:1:0.3349$].

β-Lævulose penta-acetate, well-formed, rhombic, bisphenoidal crystals from ether [$a:b:c = 0.4941:1:0.9094$].

The two substances exhibit the same symmetry and one identical ratio. This ratio, $a:b$, is probably determined by a cyclic atomic structure common to both. The substances are not interconvertible, and this kind of morphotropic relationship must be caused by true chemical isomerism, in which a great part of the molecule is common to both modifications.

E. H. R.

Attempts at the Biochemical Synthesis of Diglucosides of Multivalent Alcohols. β-Diglucoside of Glycol. ÉM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1917, **165**, 728—730). —It is shown that, by the action of emulsin on an aqueous solution of dextrose (2 mols.) and ethylene glycol (1 mol.), a mixture of glucosides and hexobioses is formed, but it was not possible to isolate the former in a crystalline state or to determine whether they were diglucosides.

W. G.

The Synthesis of Two New Disaccharides and their Biological Behaviour. FRITZ WREDE (*Biochem. Zeitsch.*, 1917, **83**, 96—102).—By the action of potassium sulphide or selenide on alcoholic solutions of β-acetobromodextrose, the octa-acetates of disaccharides are obtained, in which one of the oxygen atoms is replaced by sulphur or selenium.

These well-crystallised substances yield on hydrolysis by acids hydrogen sulphide or selenide and a reducing sugar. For the sulphur compound, $C_{28}H_{38}O_{18}S$, $[\alpha]_D^{?} = -38.21°$, and for the selenium compound, $C_{28}H_{38}O_{18}Se$, $[\alpha]_D^{25} = -51.24°$, in tetrachloro-

ethane solution. On hydrolysis with alcoholic ammonia, scission of the acetyl groups takes place, and the *disaccharides*, $C_{12}H_{22}O_{10}S$, m. p. 174°, $[\alpha]_D^{26} = -86.74°$ (in water), and $C_{12}H_{22}O_{10}Se$, m. p. 193°, $[\alpha]_D^{27} = -83.58°$, are obtained. The sugars yield crystalline metallic salts, such as the potassium salts, $C_{12}H_{21}O_{10}Se$(or S)$K + 2H_2O$ and $C_{12}H_{20}O_{10}Se$(or S)$K_2 + 4H_2O$. The sugars are only very slightly toxic, and pass through the body of mice for the most part unchanged. The sugars are very resistant to the actions of enzymes. They are designated, for reasons given by the author, as *thio-* and *seleno*-iso*trehalose*. S. B. S.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. III. Racemic and Optically Active Complex Salts of Tervalent Rhodium. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 244—262).—In continuation of previous investigations on the complex triethylenediamine salts of cobalt (A., 1915, ii, 399), corresponding salts of rhodium have now been examined crystallographically.

Sodium rhodium chloride, $\{RhCl_6\}Na_3,12H_2O$, forms blackish-red, massive, apparently octahedral crystals belonging to the monoclinic system [$a:b:c = 1.2034:1:1.4576$; $\beta = 57°9\frac{1}{2}'$].

r-Triethylenediaminerhodium chloride, $[Rh(C_2H_8N_2)_3]Cl_3,3H_2O$, forms strongly refracting prisms of ditetragonal scalenohedral symmetry [$a:c = 1:0.6730$]. The substance is perfectly isomorphous with the corresponding cobalti-salt, Werner's supposition that it is cubic, forming mixed crystals with sodium chloride, being erroneous.

r-Triethylenediaminechromi-chloride, $[Cr(C_2H_8N_2)_3]Cl_3,3H_2O$, forms orange, transparent, lustrous prisms, isomorphous with the previous compound [$a:c = 1:0.6930$].

l-Triethylenediaminerhodium chloro-*d*-tartrate,

$$[Rh(C_2H_8N_2)_3]Cl(C_4H_4O_6),4H_2O,$$

colourless, monoclinic plates or prisms [$a:b:c = 0.9158:1:0.6965$; $\beta = 72°35\frac{3}{4}'$].

l-Triethylenediaminerhodium bromide, $[Rh(C_2H_8N_2)_3]Br_3,2H_2O$, colourless ditetragonal, apparently bipyramidal, prisms, isomorphous with the corresponding cobalti-salt [$a:c = 1:0.8330$]. No indication of hemihedrism was observed.

r-Triethylenediaminerhodium iodide, $[Rh(C_2H_8N_2)_3]I_3,H_2O$, small, colourless, rhombic bipyramidal crystals, isomorphous with the corresponding cobalti-salt [$a:b:c = 0.8541:1:0.8632$].

l-Triethylenediaminerhodium iodide, $[Rh(C_2H_8N_2)_3]I_3,\frac{1}{2}H_2O$ (?), is undoubtedly isomorphous with the corresponding cobalti-salt, although this contains one molecule of water of crystallisation. The small, well-developed crystals are rhombic [$a:b:c = 0.8064:1:0.7380$], but the expected bisphenoidal character is not exhibited in any distinct way, any more than in the case of the optically active cobalti-salt.

r-Triethylenediaminerhodium nitrate, $[Rh(C_2H_8N_2)_3](NO_3)_3$, is

isomorphous with the cobalti-salt, rhombic pyramidal [$a:b:c=$ 0·7874 : 1 : 0·5606]. The crystals are always distinctly hemimorphic, a being the polar axis.

l-Triethylenediaminerhodium nitrate, also isomorphous with the cobalti-salt, forms rhombic crystals, variously distorted and distinctly bisphenoidal in character [$a:b:c=$ 0·8642 : 1 : 0·6049].

Tables and curves showing the optical rotations and dispersions of solutions of the optically active salts are given. The dispersion curves for the rhodium salts are very different in shape from those of the cobalti-salts, whilst the absolute rotation values are much greater for the latter.

The optically active salts do not in general exhibit the hemihedral characters which would be anticipated from a rigid application of Pasteur's principle. It is concluded that chemical identity of the asymmetrically arranged substituents around the central atom is unfavourable for the development of enantiomorphism in the crystals. The asymmetry as such chiefly determines the size of the optical rotation, whilst chemical contrast between the different substituents determines the manifestation of crystal enantiomorphism.

A great deal of evidence is advanced that, contrary to Werner's view, the same configuration must be attributed to corresponding optically active complex salts of cobalt and rhodium when these exhibit a rotation in the same direction. E. H. R.

Some Isomeric Complex *cis*- and *trans*-Diethylenediamine Salts of Cobalt, and Triethylenediamine Zinc Chloride. F. M. Jaeger and Jul. Kahn (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 292—303).—According to Werner's theory, compounds containing complex ions of the type ($MeX_4'Y_2'$) must exist in two isomeric forms, of which the *cis*-form alone is resolvable into optical antipodes. Several *cis*- and *trans*-isomerides are here described crystallographically.

r-cis-Diamminodiethylenediaminecobaltichloride,

$$[Co(NH_3)_2(C_2H_8N_2)_2]Cl_3,H_2O,$$

reddish-brown, lustrous plates, isomorphous with the corresponding bromide and iodide. Monoclinic prismatic [$a:b:c=$ 1·1172 : 1 : 0·8325; $\beta=87°56\frac{1}{3}'$]. The bromide has [$a:b:c=$ 1·1177 : 1 : 0·8322; $\beta=88°5'$], and the iodide [$a:b:c=$ 1·0975 : 1 : 0·8178; $\beta=87°28\frac{2}{3}'$]. The crystals of all three salts are weakly dichroic.

trans-Diamminodiethylenediaminecobalti-iodide, small, ill-developed, hexagonal-shaped plates, rhombic bipyramidal [$a:b:c=$ 1·2449 : 1 : 1·2842].

r-cis-Diamminodiethylenediaminecobaltinitrate,

$$[Co(NH_3)_2(C_2H_8N_2)_2](NO_3)_3,$$

well-formed, reddish-brown pyramids, rhombic bipyramidal [$a:b:c=$ 0·9473 : 1 : 0·6758].

r-cis-Dinitrodiethylenediaminecobaltinitrate,

$$[Co(NO_2)_2(C_2H_8N_2)_2](NO_3),$$

small, yellowish-red prisms, monoclinic prismatic [$a:b:c=1\cdot5589:1:0\cdot4073$; $\beta=68°30\frac{3}{4}'$].

trans-Dinitrodiethylenediaminecobaltinitrate, from the mother liquor of the *cis*-isomeride, forms well-developed, lustrous, reddish-brown crystals, monoclinic prismatic [$a:b:c=1\cdot3040:1:1\cdot0085$; $\beta=73°31\frac{1}{4}'$].

r-*cis*-Dinitrodiethylenediaminecobaltinitrite,

$$[Co(NO_2)_2(C_2H_8N_2)_2](NO_2),$$

well-developed, dark crystals, monoclinic prismatic [$a:b:c=0\cdot7382:1:0\cdot9094$; $\beta=82°57'$]. The corresponding *trans*-isomeride contains $2H_2O$, and forms large, well-developed prisms, which quickly effloresce. It is monoclinic prismatic [$a:b:c=1\cdot0458:1:1\cdot7995$; $\beta=68°33\frac{2}{3}'$]. From a solution containing both *cis*- and *trans*-isomerides, crystals are obtained intermediate between those of the two pure individuals [$a:b:c=1\cdot0169:1:0\cdot9030$; $\beta=66°16'$]. The ratio $a:b$ is similar to that of the *trans*-, whilst $b:c$ resembles that of the *cis*-isomeride. It is not clear whether a double compound or a mixed crystal is formed.

r-Triethylenediaminezinc chloride, $[Zn(C_2H_8N_2)_3]Cl_2,2H_2O$, forms lustrous, transparent crystals, monoclinic prismatic [$a:b:c=0\cdot9238:1:0\cdot6299$; $\beta=86°33'$]. Attempts to resolve the racemic compounds are being made. E. H. R.

The Catalytic Reduction of ω-Nitrostyrenes. ADOLF SONN and ALBERT SCHELLENBERG (*Ber.*, 1917, **50**. 1513—1525).—On reduction in alcoholic suspension with a molecular proportion of hydrogen in the presence of platinum-black, ω-nitrostyrene is converted into a mixture of isomeric, probably stereoisomeric, compounds of the composition $C_{16}H_{16}O_4N_2$; the less soluble product is *αδ-dinitro-βγ-diphenylbutane*, $NO_2\cdot CH_2\cdot CHPh\cdot CHPh\cdot CH_2\cdot NO_2$, hexagonal prisms, m. p. 238° (decomp.) [*sodium* derivative, $C_{16}H_{14}O_4N_2Na_2$; *tetrabromo*-derivative, $C_{16}H_{12}O_4N_2Br_4$, colourless prisms, m. p. 219° (decomp.); *bisphenylhydrazone*, of the corresponding butanedione, $C_2H_2Ph_2[C(NO_2)\colon N\cdot NHPh]_2$, orange-red prisms, m. p. 213—214° (decomp.), obtained by the action of benzenediazonium acetate on the solution of the nitro-compound in methyl alcohol containing sodium methoxide], the constitution of which is confirmed by oxidation of the sodium derivative with potassium permanganate to *β*-*s*-diphenylsuccinic acid. The accompanying *isomeride*, pearly scales, m. p. 190° (decomp.), is obtained in small quantity, but its stereoisomeric nature is assumed by analogy with the results with the corresponding reduction products of ω-nitro-3:4-methylenedioxystyrene; the two dinitrodiphenylbutanes are distinguished by the prefixes *α*- and *β*-. If the ω-nitrostyrene is reduced similarly, but in acetic acid instead of alcohol, the chemical change is more vigorous and proceeds somewhat differently, only the *α*-modification of the dinitrodiphenylbutane being obtained, together with phenylacetaldoxime and an amorphous mixture of substances.

ω-Nitro-3:4-methylenedioxystyrene, when reduced in alcoholic

suspension by hydrogen and platinum-black yields the α- and β-modifications of *αδ-dinitro-βγ-bis[-3 : 4-methylenedioxyphenyl]-butane*, $NO_2\cdot CH_2\cdot CH(C_6H_3{:}O_2{:}CH_2)\cdot CH(C_6H_3{:}O_2{:}CH_2)\cdot CH_2\cdot NO_2$; the α-form crystallised in prisms, m. p. 249° (decomp.) (*disodium* derivative, $C_{18}H_{14}O_8N_2Na_2$; *tetrabromo*-derivative, $C_{18}H_{12}O_8N_2Br_4$, needles, m. p. 201° (decomp.); *bisphenylhydrazone* of the corresponding butanedione,

$$\begin{array}{l} CH_2{:}O_2{:}C_6H_3\cdot CH\cdot C(NO_2){:}N\cdot NHPh \\ CH_2{:}O_2{:}C_6H_3\cdot CH\cdot C(NO_2){:}N\cdot NHPh' \end{array}$$

leaflets, m. p. 209° with decomp., obtained by the action of benzenediazonium acetate on the disodium compound). The disodium derivative in aqueous solution was oxidisable by potassium permanganate, with formation of s-*di(-3 : 4-methylenedioxyphenyl)-succinic acid*, $CH_2{:}O_2{:}C_6H_3\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot C_6H_3{:}O_2{:}CH_2$, colourless prisms, m. p. 259° (decomp.), of which the *tin, lead, mercury, bismuth*, and *silver* salts were prepared by precipitation. The *β-stereoisomeride*, $C_{18}H_{16}O_8N_2$, pale yellow rhombic tablets, m. p. 173° (decomp.), like the α-compound, forms a *tetrabromo*-derivative, $C_{18}H_{12}O_8N_2Br_4$, pale yellow tablets or prisms, and a *disodium* derivative, $C_{18}H_{14}O_8N_2Na_2$, which reacts with benzenediazonium acetate, yielding a *bisphenylhydrazone*, $C_{30}H_{24}O_8N_6$, needles, m. p. 186°.

Reduction of ω-nitro-3 : 4-methylenedioxystyrene in alcohol by hydrogen and colloidal palladium also gives the α- and β-modifications of dinitrodi(methylenedioxyphenyl)butane, whilst reduction in acetic acid with hydrogen and platinum yields the α-stereoisomeride, together with homopiperonaldioxime and resinous products. D. F. T.

Derivatives of *n*-Butylaniline. JOSEPH REILLY and WILFRID JOHN HICKINBOTTOM (T., 1917, **111**, 1026—1034).—*n*-Butylaniline has been obtained by heating together aniline and *n*-butyl chloride, and converted by well-known methods into the following series of compounds: *A*, phenyl-*n*-butylnitrosoamine, phenyl-*n*-butylhydrazine, and diphenyldi-*n*-butyltetrazone, $C_6H_5\cdot N(C_4H_9)\cdot NO \longrightarrow C_6H_5\cdot N(C_4H_9)\cdot NH_2 \longrightarrow C_4H_9\cdot NPh\cdot N{:}N\cdot NPh\cdot C_4H_9$; *B*, *p*-nitroso-*n*-butylaniline, *p*-phenylene-*n*-butyldiamine, and *p*-nitrosophenyl-*n*-butylnitrosoamine, $NH_2\cdot C_6H_4\cdot NH\cdot C_4H_9 \longleftarrow NO\cdot C_6H_4\cdot NH\cdot C_4H_9 \longrightarrow NO\cdot C_6H_4\cdot N(C_4H_9)\cdot NO$.

For experimental details, see original. J. C. W.

Bromides of Schiff's Bases. HARTWIG FRANZEN, HENRYK WEGRZYN, and MEER KRITSCHEWSKY (*J. pr. Chem.*, 1917, [ii], **95**, 374—391. Compare A., 1914, i, 162; 1915, i, 230; 1917, i, 644). —In earlier papers, it has been shown that the dibromides of Schiff's bases suffer rearrangement into benzylidene-*p*-bromoanilines when boiled with alcohol or treated with pyridine. Frequently, it was found that the original dibromides contained an excess of halogen, and consequently gave mixed products on rearrangement.

has therefore been investigated more closely. These Schiff's bases have been dissolved in various media, the solutions cooled by ice, and bromine slowly added in the pure or diluted state, equimolecular quantities being employed. The precipitates have then been collected and analysed.

With ether and carbon disulphide alone is it possible to obtain pure products, and with these, dibromides and tribromides are formed. The dibromides can only have the formula

$$CHPhBr{\cdot}NRBr,$$

but the constitution of the tribromides remains in doubt. The extra bromine atom is not attached to one of the nuclei, neither has it replaced hydrogen in the –CHPh– grouping. It appears to be attached to nitrogen, as in the perhaloids of tertiary amines.

Ethereal Solution.—Benzylideneaniline gives with undiluted bromine the bright yellow *tribromide*, $C_{13}H_{11}NBr_3$, m. p. 156—157° (decomp.), and some of the lemon-yellow dibromide, m. p. 203—207°, which separates from the first filtrate. If the bromine is diluted with carbon disulphide, the dibromide only is precipitated. Benzylidene-*p*-toluidine gives a deep yellow *tribromide*, $C_{14}H_{13}NBr_3$, golden-yellow leaflets, m. p. 168—172°, under both conditions.

Carbon Disulphide Solution.—Benzylideneaniline yields the pure dibromide, and benzylidene-*p*-toluidine the pure tribromide.

Benzene Solution.—Benzylideneaniline forms a brick-red dibromide, containing bromine in excess of the theoretical amount; benzylidene-*p*-toluidine gives the tribromide.

Chloroform Solution.—Benzylideneaniline gives a mixture of di- and tri-bromide; benzylidene-*p*-toluidine forms in dilute solutions a yellow powder, containing more bromine than a tetrabromide, and in more concentrated solutions a mixture of di- and tribromide.

Light Petroleum Solution.—Benzylideneaniline deposits a bright brick-red powder, containing somewhat less bromine than the dibromide; benzylidene-*p*-toluidine gives a similar reddish-yellow powder.

Glacial Acetic Acid Solution.—Benzylideneaniline forms a mixture of mono- and di-bromides.

Benzylidenebenzylamine, in chloroform solution, also yields a brick-red *tribromide*, m. p. 149°. This reacts with aqueous ammonia according to the scheme: $C_{14}H_{13}NBr_3 \longrightarrow C_6H_5{\cdot}CN + NH_2{\cdot}CH_2Ph + NH_4Br$. The absence of brominated benzene derivatives among the products is evidence that the third bromine atom in these tribromides is not attached to a benzene nucleus. The compound liberates one atomic proportion of iodine from acidified potassium iodide. J. C. W.

The Reciprocal Exchange of Aromatically Combined Hydroxyl and Halogen. W. BORSCHE [with HUGO LÖWENSTEIN [illegible]

paper (A., 1917, i, 15), it was shown that the *p*-nitro group in halogeno-2:4-dinitrobenzene can be substituted by the cyano, acetyl, or benzoyl group without seriously lessening the reactivity of the halogen atom. It has now been tested whether these groups can replace one of the nitro-groups in dinitrophenols without hindering the exchange of the hydroxyl group by chlorine in Ullmann's reaction (A., 1908, i, 524). Even in the least unfavourable case, namely, when a cyano-group is in the para-position of an *o*-nitrophenol, the replaceability of the hydroxyl group is considerably lessened.

When 3-nitro-4-hydroxybenzonitrile is heated with *p*-toluenesulphonyl chloride and diethylaniline, a considerable quantity of the p-*toluenesulphonate*, $NO_2\cdot C_6H_3(CN)\cdot O\cdot SO_2\cdot C_6H_4Me$, is obtained, in pale yellow leaflets, m. p. 139—141°, but about 5% of 4-chloro-3-nitrobenzonitrile is formed. This is identified by conversion into 2-nitro-4-cyanodiphenylamine.

5-*Nitro-4-hydroxytoluonitrile*, pale yellow needles, m. p. 132—133°, gives only the p-*toluenesulphonate*, sparkling crystals, m. p. 137—138°. This new substituted cresol is obtained as follows: *p*-homosalicylaldehyde is nitrated in cold, glacial acetic acid, the nitro-aldehyde is converted into the oxime, m. p. 214—216°, and this is boiled with acetic anhydride. The 3-*nitro-5-cyano*-p-*tolyl acetate*, m. p. 136°, so formed is hydrolysed by contact with 2% potassium hydroxide.

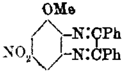
3-*Nitro-4-hydroxy-5-methoxybenzonitrile*, white needles, m. p. 140°, also only yields the p-*toluenesulphonate*, m. p. 104°. The new substituted guaiacol is prepared as follows: acetylvanillonitrile is slowly added to well-cooled, fuming nitric acid, and the product, 2-*nitro-4-cyano-6-methoxyphenyl acetate*, slender, pale yellow needles, m. p. 102°, is hydrolysed.

Comparing 3-nitro-4-hydroxybenzonitrile with 3-nitro-4-hydroxy-5-methoxybenzonitrile, it appears, therefore, that the mobility of the hydroxyl group, which is already much less than it is in the case of 2:4-dinitrophenol, is completely suppressed by the proximity of the methoxy-group. In the case of dinitroguaiacol, however, the methoxy-group does not exert such an influence. When this compound (4:6-dinitro-2-methoxyphenol) is treated with *p*-toluenesulphonyl chloride and sodium carbonate, it yields the p-*toluenesulphonate*, prisms, m. p. 137—138°, but it reacts with the chloride in the presence of diethylaniline to give, in addition to a small amount of this ester, 2-*chloro-3:5-dinitroanisole*,

$$OMe\cdot C_6H_2Cl(NO_2)_2,$$

which crystallises in greenish-yellow leaflets, m. p. 93—94°. This chloride has been converted by the usual methods into the following compounds: (*A*) 4:6-*dinitro-2-methoxydiphenylamine*, golden-yellow needles, m. p. 156°; (*B*) 3:5-*dinitro-o-anisidine*, orange-coloured needles, m. p. 176°, which may be reduced by ammonium sulphide to 5-*nitro-2-methoxy-o-phenylenediamine*, dark red needles, m. p. 131—132°, and then condensed with benzil to form 7-*nitro-*

5-*methoxy*-2 : 3-*diphenylquinoxaline* (annexed formula), in yellow needles, m. p. 207—208°; (*C*) 6-*nitro*-4-*methoxy*-2-*phenyl*-ψ-*aziminobenzene*,



$$NO_2\cdot C_6H_2(OMe)<\begin{matrix}N\\|\\N\end{matrix}>NPh,$$

sulphur-yellow, felted needles, m. p. 191°; (*D*) *ethyl* 4 : 6-*dinitro*-2-*methoxyphenylmalonate*, stout, yellow crystals, m. p. 68—69°, which may be hydrolysed by dilute sulphuric acid to 4 : 6-*dinitro*-2-*methoxyphenylacetic acid*, pale brown needles, m. p. 174—175° (evolution of carbon dioxide), *methyl* ester, m. p. 68—69°.

The usual methods for the replacement of halogen by hydroxyl in halogenonitrobenzenes leave much to be desired. Alkali hydroxides are out of the question when cyano, acetyl, carboxylic ester, or similar groups are present, and metallic acetates react so sluggishly. Heating with anhydrous sodinm acetate and acetamide at 170—200°, however, often gives excellent results, and several applications of this method are now described.

1-Chloro-2 : 4-dinitrobenzene is unattacked by water at 200°, or by crystallised sodium acetate in an open vessel at 210°. When heated with 25% sodium acetate solution in a sealed tube at 200°, it is soon completely converted into 2 : 4-dinitrophenol. It only reacts with silver acetate, also in the presence of water, at 200°, giving the phenol and a small quantity of a substance, m. p. 216° (decomp.), which is most probably 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether.

1-Chloro-2 : 6-dinitrobenzene gives an almost quantitative yield of 2 : 6-dinitrophenol when heated with anhydrous sodium acetate and acetamide at 170°, and 3-chloro-4 : 6-dinitrotoluene gives 4 : 6-dinitro-*m*-cresol, mixed with considerable quantities of amorphous products, due to reactions between the adjacent nitro and methyl groups.

1 : 3-Dichloro-4 : 6-dinitrobenzene reacts with 25% sodium acetate solution at 190—195°, or with the acetamide mixture at 160°, to give 3-*chloro*-4 : 6-*dinitrophenol*, in flat, yellow needles, m. p. 92°. At higher temperatures, complete decomposition sets in, and no dinitroresoroinol can be isolated from the product.

5-Chloro-2 : 4-dinitroanisole, from 1 : 3-dichloro-4 : 6-dinitrobenzene and sodium methoxide solution, reacts with the acetamide mixture to form 4 : 6-dinitro-3-methoxyphenol.

3-Chloro-4 : 6-dinitrodiphenyl ether, from 1 : 3-dichloro-4 : 6-dinitrobenzene and potassium phenoxide, reacts with aniline to form 4 : 6-*dinitro*-3-*phenoxydiphenylamine*, elongated, orange-red rhombs, m. p. 151·5°, and with the above mixture to give 4 : 6-*dinitro*-3-*phenoxyphenol*, flat, brownish-yellow needles, m. p. 117—118°.

1 : 3-Dichloro-4 : 6-dinitrobenzene reacts with alcoholic dimethylamine solution to give a mixture of 4 : 6-*dinitrotetramethyl*-*m*-*phenylenediamine* and 3-chloro-4 : 6-dinitrodimethylaniline, which are very difficult to separate. Only the latter reacts with the

acetamide mixture, however, and the product is easily separated by ammonia solution into the diamine, yellow needles, m. p. 191°, and 4 : 6-*dinitro-3-hydroxydimethylaniline*, dark yellow needles, m. p. 152°. [Lippmann and Fleissner's compound, m. p. 195°, is really 2 : 4-*dinitro-3-hydroxydimethylaniline* (A., 1885, 1212)]. Pure 3-*chloro-4 : 6-dinitrodimethylaniline*, long, yellow needles, m. p. 129°, is prepared by heating the dichlorodinitrobenzene with an alcoholic solution of dimethylamine and glacial acetic acid.

5-Chloro-2 : 4-dinitrophenyl-1′-piperidine (A., 1914, i, 30) yields 4 : 6-*dinitro-3-hydroxyphenyl-1′-piperidine*, $C_5H_{10}N\cdot C_6H_2(NO_2)_2\cdot OH$, in stout, orange-red crystals, m. p. 100—101°.

3-Chloro-4 : 6-dintrodiphenylamine gives 4 : 6-*dinitro-3-hydroxydiphenylamine*, in bundles of long, dark yellow needles, m. p. 139°; 4-bromo-3-nitrobenzonitrile also readily yields 3-nitro-4-hydroxybenzonitrile; 4-bromo-3-nitroacetophenone reacts less readily, but gives 3-*nitro-4-hydroxyacetophenone*, slender needles, m. p. 130°; 4-bromo-3-nitrobenzophenone changes smoothly into 3-*nitro-4-hydroxybenzophenone*, which crystallises in yellowish-brown rhombs, m. p. 120—121°.

In the above reactions, the acetamide merely plays the part of a most suitable solvent with high b. p., and a source of water for the hydrolysis of the acetates obtained by the interaction of the sodium acetate and the halogen compounds. Its behaviour as a hydrolytic agent is exemplified further by the facts that 2 : 4-dinitrophenyl acetate is converted into 2 : 4-dinitrophenol, and 2 : 4-dinitroacetanilide into 2 : 4-dinitroaniline, by heating with acetamide at 200°. J. C. W.

β-Methylated Cinnamic Acids. S. Lindenbaum (*Ber.*, 1917, **50**, 1270—1274).—The author has had occasion to prepare β-methylcinnamic acids in recent years, and had used the identical method which Stoermer, Grimm, and Laage described recently (A., 1917, i, 647). An acetophenone is mixed with ethyl bromoacetate and zinc in benzene, whereby an ethyl β-hydroxy-β-arylbutyrate, $OH\cdot CMeAr\cdot CH_2\cdot CO_2Et$, is formed. In many cases, this loses water on distillation, but a preliminary boiling with phosphoryl chloride in benzene ensures this. In the cases of acetophenone itself, and o-methoxyacetophenone, the primary hydracrylates can be isolated in a pure state, but substituents in the para-position (for example, methyl, and especially methoxyl) lower the stability of these esters.

Four examples of the reaction are described, but the products were described by Stoermer and earlier workers. J. C. W.

Steric Hindrance. S. Reich [and (Mme.) R. Salzmann and D. Kawa] (*Bull. Soc. chim.*, 1917, [iv], **21**, 217—225).—The reactivity of the three di-ortho-substituted aldehydes, 2 : 6-dinitrobenzaldehyde, 2 : 6-dichlorobenzaldehyde, and 2 : 4 : 6-trimethylbenzaldehyde, increases as the weight of the substituent group increases. With 2 : 6-dichlorobenzaldehyde, an intermediate product, 2 : 6-*di-*

chlorobenzylidene diacetate, needles, m. p. 85°, can be isolated, which by the further action of sodium acetate and acetic anhydride at 180° yields 2:6-*dichlorocinnamic acid*, slender needles, m. p. 184°, from which by the action of bromine in acetic acid, *αβ-dibromo-β-2:6-dichlorophenylpropionic acid*,

$$C_6H_3Cl_2\cdot CHBr\cdot CHBr\cdot CO_2H,$$

m. p. 184°, is obtained. This acid yields, with alcoholic potassium hydroxide, 2:6-*dichlorophenylpropiolic acid*, $C_6H_3Cl_2\cdot C\vdots C\cdot CO_2H$, m. p. 167—168°, and 2:6-*dichlorophenylacetylene*, $C_6H_3Cl_2\cdot C\vdots CH$, m. p. 100°. These on bromination give respectively *αβ-dibromo-2:6-dichlorophenylacrylic acid*, m. p. 171—172°, and *αβ-dibromo-2:6-dichlorophenylstyrene*, m. p. 70—71°.

The ease of esterification of benzoic acid is decreased one hundred and sixty-three times by the introduction of two chlorine atoms into the ortho-positions, whilst the reactivity of ethyl benzoate towards magnesium phenyl bromide is only diminished fourteen times by a similar introduction of chlorine atoms. On the other hand, 2:6-dichlorobenzaldehyde easily reacts with Grignard's reagent, giving 2:6-*dichlorodiphenylcarbinol*,

$$C_6H_3Cl_2\cdot CHPh\cdot OH,$$

m. p. 57°, giving an *acetate*, m. p. 105°.

The two di-ortho-substituted anilines, 2:4:6-trinitro- and 2:4:6-tribromo-aniline, do not condense with benzaldehyde (compare Hantzsch, A., 1891, 68), but 2:6-dinitro- and 2:6-dichlorobenzaldehyde both condense readily with aniline. 2:6-*Dichlorobenzylideneaniline* crystallises in pale yellow needles, m. p. 64—65°.

2:6-Dichlorobenzaldehyde gives an o-*nitrophenylhydrazone*, red needles, m. p. 154°, a p-*bromophenylhydrazone*, brown needles, m. p. 142°, and an *oxime*, colourless needles, m. p. 146—147°. The last compound, when boiled with acetic anhydride for five minutes, gives 2:6-*dichlorobenzonitrile*, m. p. 143° [the compound, m. p. 49°, described by Claus and Stavenhagen (compare A., 1892, 1206) under this name is not this nitrile], which is only very slightly hydrolysed by heating for three hours with 60% sulphuric acid at 150°. With hydrogen peroxide in alkaline solution, it yields 2:6-*dichlorobenzamide*, m. p. 202°. Schultz (compare this Journal, 1872, 1005) describes such a compound, m. p. 166°, but the dichlorobenzoic acid with which he started did not possess the properties now ascribed to 2:6-dichlorobenzoic acid. W. G.

Nitration of Benzoylformic [Phenylglyoxylic] Acid. S. REICH and P. MOREL (*Bull. Soc. chim.*, 1917, [iv], **21**, 225—226).—When phenylglyoxylic acid is slowly added to nitric acid (D 1·5) at −10°, the sole product is *m*-nitrophenylglyoxylic acid. W. G.

Keto-Enol Isomerism. III. The Isomeric Formylphenylacetic Esters. W. DIECKMANN (*Ber.*, 1917, **50**, 1375—1386. Compare A., 1916, i, 820, 822; and Wislicenus, A., 1917, i, 268).—Recent researches have revealed the fact that ethyl formyl-

and a solid enol, "γ," m. p. 110°, and that the methyl ester likewise exists only as an "α"-enol, m. p. 40—41°, and a "γ"-enol, m. p. 105° (in Jena glass capillaries; in soft glass, the m. p. may be as low as 70°, and a trace of sodium acetate will depress it to about 40°). Wislicenus suggested that these pairs of enols may be *cis-trans*-isomerides, although the γ-enols do not give the ferric chloride reaction or form a sparingly soluble copper salt. This objection is met by reference to dimethyldihydroresorcinol, which is certainly enolic, but does not give the ferric chloride reaction. There are steric hindrances in each case against the formation of "conjugated enol salts." The sodium salt of the α-enol is stable in the dry state, but changes into the isomeride in aqueous solution. If the aqueous solution is quickly acidified, the γ-form is obtained, but if acid is slowly added, the alkali salt still present catalyses the transformation of the γ-form into the α-modification.

The equilibria existing between the enols and the aldo-forms, which have not been isolated as yet, have been studied by Meyer's method. Distilled ethyl α-formylphenylacetate, or the liquid obtained by heating the γ-ester at 110°, is about 91% enol; the solid γ-ester is pure enol. Crystalline methyl α-formylphenylacetate is 97·4% enol, and, after melting, remains molten at the ordinary temperature, with 87% enol; the crystalline γ-ester is pure enol. After heating at 110° for three hours, the α-ethyl ester drops to 78—81% enol, but reaches the above equilibrium when kept.

The crystalline ethyl ester is present in 1% solutions in pure formic acid, acetic acid, benzene, and hexane to the extent of 77·8, 88·6, and 97% respectively in the enolic form. In methyl alcohol, however, the esters appear to exist only to the extent of about 8% as enols, and in ethyl alcohol only 22%, but this is due to the formation of additive compounds with the solvents (compare Wislicenus). The speed of the reaction with alcohols can be ascertained by the titration method. It is about seven times as great for the γ-esters as for the α-esters, and about 1·7 times as great for methyl alcohol as for ethyl alcohol; it is greatly accelerated, in the same degree, by hydrogen chloride, which has no pronounced effect on the transformation of one enol into the other. Alkaline agents and pyridine also catalyse the reaction with alcohol in proportion to their "alkalinity," but they soon bring the speed of the reaction to the same level for both α- and γ-esters. Accordingly, alkaline agents expedite the transformation of γ- into α-forms, most probably through the aldo-modifications.

Ethyl formylphenylacetate (α or γ) does not give a colour with concentrated sulphuric acid and thiophen-benzene until it has been exposed to the air, when it gives the red to deep blue colour characteristic of phenylglyoxylic acid. Auto-oxidation does, indeed, take place according to the equation $OH\cdot CH:CPh\cdot CO_2R + O_2 = C_6H_5\cdot CO\cdot CO_2R + H\cdot CO_2H$, and the presence of the phenylglyoxylate in the product may be fully established (hydrazone; free acid and its *silver* salt, hydrazone and anil). Oxidation to phenyl-

glyoxylic acid is also immediately brought about by alkaline permanganate (compare Michael, A., 1912, i, 861).

The esters are decomposed by boiling with 90% acetic acid into the alcohol, carbon dioxide, and phenylacetaldehyde, which may be identified as the semicarbazone. J. C. W.

Semicarbazones of α-Ketonic Acids. α-Iodocinnamic Acids; αα-Di-iodo- and Dibromo-phenylbutyric Acids; α-Iodo- and α-Bromo-phenylcrotonic Acids. J. BOUGAULT (*Bull. Soc. chim.*, 1917, [iv], **21**, 246—258).—The first part of the paper is a more detailed account of work already published (compare A., 1916, i, 817; 1917, i, 26, 647). *α-Iodo-γ-hydroxy-βγ-diphenylcrotonic acid*, HO·CHPh·CPh:CI·CO_2H, m. p. 190°, is obtained by the action of iodine on an alkaline solution of the semicarbazone of α-keto-βγ-diphenylbutyrolactone, there being no intermediate formation of a di-iodo-acid and only the one α-iodo-acid. This acid when reduced with zinc and acetic acid gives a mixture of *γ-hydroxy-βγ-diphenylcrotonic acid*, m. p. 161°, and diphenylcrotonolactone, m. p. 151°. *α-Bromo-γ-hydroxy-βγ-diphenylcrotonic acid*, m. p. 192°, is similarly prepared using an alkaline solution of sodium hypobromite.

By the hydrolysis of *αα*-dibromophenylbutyramide and of *αα*-dibromophenylpropionamide with hydrochloric acid, the author has obtained respectively *αα*-dibromophenylbutyric acid and α-bromocinnamic acid. W. G.

The Phenylsuccinic Acid Series. V. Interconversion of the Esters of *r*- and *meso*-Diphenylsuccinic Acids. HENRY WREN and CHARLES JAMES STILL (T., 1917, **111**, 1019—1025. Compare A., 1917, i, 456).—The interconvertibility of *r*- and *meso*-diphenylsuccinic acids has been known for some years. It is now shown, at the instance of the methyl and ethyl compounds, that the esters readily undergo mutual transformation. Interconversion may be effected by hydrolysis with an insufficiency of alcoholic potassium hydroxide solution or by the action of a solution of the corresponding sodium alkyloxide in the requisite alcohol, or, in some instances, by the action of a suspension of sodium alkyloxide in dry ether.

meso-Diphenylsuccinic acid is slowly converted into the *r*-acid by prolonged treatment with an excess of boiling aqueous alcoholic potassium hydroxide solution, but the reverse change could not be shown to occur. H. W.

Action of Organo-magnesium Compounds on Apiolealdehyde. Preparation of Apiolealdehyde. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1917, **50**, 1335—1339).—Some years ago, the authors found that asarylaldehyde reacts with organo-magnesium compounds to give, not the usual carbinols, but their ethers (A., 1906, i, 424). The closely related apiolealdehyde yields both classes of derivatives, according to the conditions of the reaction.

Apiolealdehyde (4:5-dimethoxy-2:3-methylenedioxybenzaldehyde)

is best prepared by oxidising *iso*apiole with ethyl nitrite and hydrochloric acid. Asarone is conveniently oxidised to asarylaldehyde by the same method.

For the preparation of carbinols, the Grignard reaction is carried out at a low temperature, and the magnesium compound is decomposed by just sufficient dilute acid. The ethers are formed when the reaction proceeds in warm solvents and the metallic compound is decomposed by an excess of dilnte sulphuric acid. Magnesium methyl iodide yields *α-4 : 5-dimethoxy-2 : 3-methylenedioxyphenylethyl alcohol*, m. p. 52°, and its *ether*,

$[CH_2:O_2:C_6H(OMe)_2\cdot CHMe]_2O$,

m. p. 122°; magnesium ethyl iodide gives *α-4 : 5-dimethoxy-2 : 3-methylenedioxyphenylpropyl alcohol*, m. p. 54°, and its *ether*, m. p. 112°; and *phenyl-4 : 5-dimethoxy-2 : 3-methylenedioxyphenylmethyl alcohol*, $C_9H_9O_4\cdot CHPh\cdot OH$, has m. p. 72°. J. C. W.

Some Derivatives of Propiophenone. K. von Auwers (*Ber.*, 1917, **50**, 1177—1182).—α-Bromopropiophenone has b. p. 136—137°/16 mm., D_4^{20} 1·430, n_D^{20} 1·5716, $E\Sigma_a$ +0·52, $E\Sigma_D$ +0·55, $E\Sigma_\beta - \Sigma_a$ + 37%, $E\Sigma_\gamma - \Sigma_a$ + 41%. In its reactions with bases and ketone reagents, this compound is usually just as much attacked at the bromine atom as at the carbonyl group, if not more so. With excess of alcoholic *p*-nitrophenylhydrazine hydrochloride, for example, it reacts on boiling to form the di-*p*-nitrophenylhydrazone of phenyl methyl diketone (below), but it behaves in a slightly abnormal way with one molecular proportion of the salt in alcohol at 40°. Under these conditions, a small quantity of *phenyl α-ethoxyethyl ketone* p-*nitrophenylhydrazone*,

$OEt\cdot CHMe\cdot CPh:N\cdot NH\cdot C_6H_4\cdot NO_2$,

may be isolated, in pale yellow, glassy needles, m. p. 97—98°. 3-α-Bromopropionyl-*p*-cresol reacts more readily under these conditions, giving m-*4-hydroxytolyl α-ethoxyethyl ketone* p-*nitrophenylhydrazone*, golden-yellow, flat needles, m. p. 178—180°.

α-Acetoxypropiophenone, b. p. 143—147°/17 mm., D_4^{20} 1·112, n_D^{20} 1·5153, $E\Sigma_a$ +0·53, $E\Sigma_D$ +0·53, $E\Sigma_\beta - E\Sigma_a$ +26%, is readily obtained from the bromo-compound and converted into α-hydroxypropiophenone (phenyl α-hydroxyethyl ketone), $OH\cdot CHMe\cdot COPh$. This compound was obtained by Zincke and Zahn (A., 1910, i, 317) by the oxidation of methylphenylethyleneglycol, but they were more inclined to regard it as the isomeride,

$OH\cdot CHPh\cdot COMe$.

The identity of the two preparations is fully established by optical means. The ketone has b. p. 125—126°/14 mm., D_4^{20} 1·1065, n_D^{20} 1·5355, $E\Sigma_a$ +0·37, $E\Sigma_D$ +0·38, $E\Sigma_\beta - \Sigma_a$ +24% (averages), and forms a semicarbazone, m. p. 188—189°. With *p*-nitrophenylhydrazine hydrochloride and alcohol in the cold, it forms the p-*nitrophenylhydrazone*, orange-yellow, flat, glassy needles, m. p. 179—180°, but with an excess of the reagent in hot solutions it gives the *di-*p-*nitrophenylhydrazone* of *phenyl methyl diketone*, a dark red, crystalline powder, m. p. 256—257°. α-Hydroxypropio-

phenone, or, better still, phenyl methyl diketone, reacts with *o*-phenylenediamine in boiling acetic acid to form *3-phenyl-2-methylquinoxaline*, $C_6H_4<\begin{smallmatrix}N:CMe\\N:CPh\end{smallmatrix}$, m. p. 57—58°. J. C. W.

The Sulphonation of Chalkones [Phenyl Styryl Ketones]. (The Formation of Intramolecular Oxonium Salts.) P. PFEIFFER and P. A. NEGREANU (*Ber.*, 1917, **50**, 1465—1477).—The ease with which ketones may be sulphonated by sulphuric acid is of interest as influencing the trustworthiness of the colours observed in the formation of halochromic compounds between ketones and the acid; freshly prepared solutions of the ketones in the acid yield the unaltered ketone on dilution with water, but in some cases, such as those described below, sulphonation is sufficiently rapid to become appreciable in a few hours at the ordinary temperature.

Phenyl *p*-methoxystyryl ketone at the ordinary temperature is gradually converted by sulphuric acid into *phenyl* p-*methoxystyryl ketone-sulphonic acid*, $COPh\cdot CH:CH\cdot C_6H_3(OMe)\cdot SO_3H$, yellow needles, m. p. 160—162°, which become orange-red above 140° (*ammonium* salt, yellow needles with $1H_2O$, m. p. 261°). In a similar manner, anisyl *p*-methoxystyryl ketone is converted into *anisyl* p-*methoxystyryl ketone-sulphonic acid*,

$$OMe\cdot C_6H_4\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)\cdot SO_3H,$$

almost colourless, sometimes pale red, leaflets, m. p. indistinct near 180—181°, giving a blood-red liquid (*ammonium* salt with $2H_2O$, colourless leaflets, m. p. 279°); the constitution of this substance is demonstrated by oxidation with potassium permanganate, giving rise to a sulphoanisic acid, $OMe\cdot C_6H_3(SO_3H)\cdot CO_2H,1\frac{1}{2}H_2O$, m. p. 236° (decomp.) (potassium salt, needles with $2H_2O$), possibly identical with the compound described by Zervas (*Annalen*, 1857, **103**, 341).

Benzylidenepaeonol reacts slowly with sulphuric acid at the ordinary temperature, giving *benzylidenepaeonolsulphonic acid*, $CHPh:CH\cdot CO\cdot C_6H_2(OH)(OMe)\cdot SO_3H$, pale yellow needles with $2H_2O$, m. p. 163—164°, giving a blood-red liquid (*ammonium* salt, almost colourless needles with $2H_2O$, m. p. 256°). Phenyl anisylethyl ketone, m. p. 68° (Bargellini and Bini, A., 1911, i, 68, give 59—60°), similarly yielded *phenyl sulphoanisylethyl ketone*, $COPh\cdot CH_2\cdot CH_2\cdot C_6H_3(OMe)\cdot SO_3H$, prismatic needles with $2H_2O$, m. p. 146°; *ammonium* salt, colourless needles with $1H_2O$, m. p. 245°. *Anisyl phenylethyl ketone*, $CH_2Ph\cdot CH_2\cdot CO\cdot C_6H_4\cdot OMe$, prepared from anisyl styryl ketone by reduction in acetic acid with hydrogen and platinum-black, forms colourless leaflets, m. p 97° (*oxime*, colourless needles, m. p. 114°), and reacts slowly with sulphuric acid, with formation of *sulphoanisyl phenylethyl ketone*, $CH_2Ph\cdot CH_2\cdot CO\cdot C_6H_3(OMe)\cdot SO_3H$, colourless needles with $5H_2O$, m. p. indefinite; *ammonium* salt, colourless needles, m. p. 270—271°. *Anisyl anisylethyl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OMe$, obtained from anisyl *p*-methoxystyryl ketone in acetic acid with hydrogen and platinum-black, forms monoclinic crystals, m. p. 45°

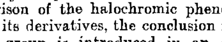
(*oxime*, colourless needles, m. p. 119°), and with sulphuric acid at the ordinary temperature gradually forms *anisyl sulphoanisylethyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}SO_3H$, colourless needles with $3H_2O$, m. p. 149°; *ammonium* salt, colourless leaflets with $\frac{1}{2}H_2O$, m. p. 278°.

Chalkone (phenyl styryl ketone) and its methoxy-derivative, *p*-methoxyphenyl styryl ketone, resisted sulphonation by sulphuric acid at the ordinary temperature.

From a comparison of the halochromic phenomena with phenyl styryl ketone and its derivatives, the conclusion is drawn that when a sulphonic acid group is introduced in an ortho-position to a methoxyl group, the halochromic colours with sulphuric or perchloric acid revert closely to those of the methoxyl-free parent compound, so that the auxochromic effect of a methoxyl group is apparently nullified by the presence of an adjacent sulphonic acid group. This is attributed to oxonium salt formation between the two groups in question. D. F. T.

Some Aromatic Keto-oxido-compounds. HENRIK JÖRLANDER (*Ber.*, 1917, **50**, 1457—1465. Compare A., 1917, i, 222).—The author has already applied Widman's reaction (A., 1916, i, 406, 655) to the preparation of such substances as anisoylphenylethylene oxide, and now extends it to the condensation of benzaldehyde with certain ω-halogen ketones, the general method of procedure being to add the calculated quantity of sodium ethoxide dissolved in alcohol to a cooled alcoholic mixture of the halogen ketone with a 20% excess of benzaldehyde.

ω-Dichloro-3:4-dimethylacetophenone and benzaldehyde gave rise to 3:4-*dimethylbenzoylphenylethylene oxide*,



colourless prisms, m. p. 89°, which on oxidation with alkaline permanganate yielded 4-methyl*iso*phthalic acid, and on treatment with alcoholic sodium hydroxide underwent the general transformation of this class of substance with formation of o-4-*xylyl α-hydroxystyryl ketone*, $C_6H_3Me_2{\cdot}CO{\cdot}C(OH){:}CHPh$, yellow prisms, m. p. 94—95°, which gave a deep violet-brown coloration with ferric chloride. Acetic anhydride with the addition of a little sulphuric acid converted the cyclic oxide into 3:4-*dimethylbenzoylphenylethylene diacetate*, $C_6H_3Me_2{\cdot}CO{\cdot}CH(OAc){\cdot}CHPh{\cdot}OAc$, colourless prisms, m. p. 105°, which when warmed with alcoholic alkali gave benzyl *o*-4-xylyl ketone, $C_6H_3Me_2{\cdot}CO{\cdot}CH_2Ph$, probably produced from the free glycol by successive dehydration and intramolecular rearrangement.

ω-Chloro-2:4-dimethylacetophenone in the usual reaction yielded 2:4-*dimethylbenzoylphenylethylene oxide*, colourless leaflets, m. p. 61°, which was converted by alcoholic sodium hydroxide into *m*-4-*xylyl α-hydroxystyryl ketone*, a yellow oil, and by acetic anhydride and a little sulphuric acid into 2:4-*dimethylbenzoyl-*

former product with *o*-phenylenediamine yielded *2-benzyl-3(2′:4′-xylyl)-quinoxaline*, $C_{23}H_{20}N_2$, colourless leaflets, m. p. 126°.

Chloroacetylmesitylene, probably on account of the ortho-methyl groups, did not follow the usual course of reaction with benzaldehyde, a molecule of water undergoing elimination instead of hydrogen chloride, the product being *mesitylyl α-chlorostyryl ketone*, $C_6H_2Me_3\cdot CO\cdot CCl\colon CHPh$, colourless prisms, m. p. 86°.

p-*Phenylbenzoylphenylethylene oxide*, $\begin{matrix}O\\|\\CHPh\end{matrix}\!>\!CH\cdot CO\cdot C_6H_4Ph$, colourless leaflets, m. p. 133—134°, and *2:4-dimethoxybenzoylphenylethylene oxide*, $\begin{matrix}O\\|\\CHPh\end{matrix}\!>\!CH\cdot CO\cdot C_6H_3(OMe)_2$, colourless prisms, m. p. 116°, were obtained by the general reaction, using *p*-chloroacetyldiphenyl and ω-chloro-2:4-dimethoxyacetophenone respectively.

By the action of aluminium chloride on a mixture of chloroacetyl chloride and *p*-chloroanisole in carbon disulphide, *5-ω-dichloro-2-methoxyacetophenone*, colourless leaflets, m. p. 91° (compare Kunckell, A., 1898, i, 254), was formed, together with a small quantity of a *substance* crystallising in needles; the former reacted with benzaldehyde and sodium ethoxide, with formation of *5-chloro-2-methoxybenzoylphenylethylene oxide*,

$$\begin{matrix}O\\|\\CHPh\end{matrix}\!>\!CH\cdot CO\cdot C_6H_3Cl\cdot OMe,$$

colourless leaflets, m. p. 157°.

5-Acetylamino-o-toluoylphenylethylene oxide,

$$\begin{matrix}O\\|\\CHPh\end{matrix}\!>\!CH\cdot CO\cdot C_6H_3Me\cdot NHAc,$$

colourless needles, m. p. 149°, was obtained from ω-chloro-5-acetylamino-2-methylacetophenone in the general manner; it reacted with alcoholic sodium hydroxide, producing *5-acetylamino-o-tolyl α-hydroxystyryl ketone*, $CHPh\colon C(OH)\cdot CO\cdot C_6H_3Me\cdot NHAc$, prisms, m. p. 130—131°, from which *3(5′-acetylaminotolyl)-2-benzylquinoxaline*, $C_{24}H_{21}ON_3$, m. p. 124—125°, was obtained. The isomeric *6-acetylamino-m-toluoylphenylethylene oxide*, colourless needles, m. p. 140°, obtained in a similar manner, underwent an unexpected reaction when treated with alcoholic sodium hydroxide solution, the primarily resulting α-diketone immediately losing a molecule of acetic acid, with formation of *3-keto-2-benzylidene-5-methyl-2:3-dihydroindole*, $C_6H_3Me\!<\!\begin{matrix}NH\\CO\end{matrix}\!>\!C\colon CHPh$, orange-red leaflets, m. p. 197°. *3-Acetylamino-p-toluoylphenylethylene oxide*, colourless needles, m. p. 152°, and *p-acetylaminobenzoylphenylethylene oxide*,

$$\begin{matrix}O\\|\\CHPh\end{matrix}\!>\!CH\cdot CO\cdot C_6H_4\cdot NHAc,$$

colourless leaflets, m. p. 157°, were prepared by means of the general process; the latter was converted by alcoholic sodium hydroxide into *p-acetylaminophenyl α-hydroxystyryl ketone*, $C_{17}H_{15}O_3N$, pale yellow prisms, m. p. 125—126°, which with *o-phenylenediamine*

yielded a 3-p-*acetylaminophenyl-2-benzylquinoxaline*, $C_{23}H_{19}ON_3$, colourless needles, m. p. 199°, and with alcoholic hydrogen chloride gave *β-chloro-γ-keto-α-hydroxy-α-phenyl-γ-p-acetylaminophenylpropane*, $NHAc·C_6H_4·CO·CHCl·CHPh·OH$, colourless leaflets, m. p. 206° (decomp.); this was easily reconverted into the cyclic oxide by sodium ethoxide in alcoholic solution.

p-*Aminobenzoylphenylethylene oxide*, $\overset{O}{\underset{CHPh}{|}}\!\!>CH·CO·C_6H_4·NH_2$, was obtained in colourless leaflets, m. p. 119°. ω-Bromo-*m*-nitroacetophenone, ω-chloro-5-nitro-4-acetylaminoacetophenone, bischloroacetylanisole, acetyl-6-chloroacetyltetrahydroquinoline, and chloroacetone when submitted to treatment with benzaldehyde and alcoholic sodium ethoxide yielded only uncrystallisable products.

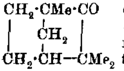
D. F. T.

Anthraquinonethioxanthone. FRITZ ULLMANN (*Ber.*, 1917, **50**, 1526).—A claim for priority against Schaarschmidt (A., 1917, i, 703).

D. F. T.

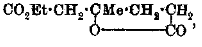
Complete Synthesis of Fenchone. L. RUZIČKA (*Ber.*, 1917, **50**, 1362—1374).—As fenchone yields such remarkably labile and somewhat obscure degradation products, it seems to be worthless to attempt to establish its formula except by a direct synthesis.

According to Semmler's formula (annexed) for fenchone, this ketone is α-methylcamphenilone. Just as lead camphenate yields camphenilone on distillation (Komppa, A., 1914, i, 556, 852), so the corresponding salt of homofenchonic acid might be expected to give fenchone. This acid has now been synthesised, but the lead salt gives a mixture of hydrocarbons on distillation, and it is doubtful whether fenchone is present in the product. It appears that the assembling of so many methyl radicles near the carboxyl group hinders the ring closure, for lead camphenate itself only gives a poor yield of camphenilone, whilst lead homo*apo*camphorate produces a fairly large amount of *apo*camphor (*ibid.*, 556).



Methyl*nor*camphor has been synthesised by methods commonly employed in this field, and by a double methylation converted into *dl*-fenchone. Semmler's formula is thus fully established.

Ethyl lævulate is condensed with ethyl bromoacetate under the influence of zinc, and the lactonic ester,



so formed (Duden, A., 1903, i, 400) is heated at 240—250° with potassium cyanide, and so converted into *ethyl β-cyano-β-methylbutane-αδ-dicarboxylate* (I), a limpid, mobile oil, b. p. 179—180°/13 mm. The crude dicarboxylate is hydrolysed by warming with

concentrated sulphuric acid and alcohol to *ethyl β-methylbutane-αββδ-tricarboxylate* (II), a mobile oil, b. p. 175—178°/12 mm.

$$\underset{\text{(I.)}}{CN\cdot CMe(CH_2\cdot CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et} \longrightarrow \underset{\text{(II.)}}{CO_2Et\cdot CMe(CH_2\cdot CO_2Et)\cdot C_2H_4\cdot CO_2Et}$$

The tricarboxylate is heated with sodium and benzene, and so condensed to 1-*methyl*cyclo*pentan*-3-*one*-1-*carboxylic acid*, a viscous oil, b. p. 170°/12 mm., which forms a *semicarbazone*, m. p. 189—190° (decomp.). The *ethyl* ester (III), b. p. 115°/12 mm., is condensed with ethyl α-bromo*iso*butyrate in the presence of zinc, yielding *ethyl 3-hydroxy-3-β-carbethoxy*iso*propyl*-1-*methyl*cyclo*pentane*-1-*carboxylate* (*ethyl hydroxyhomofenchonate*) (IV), b. p. 171—173°/12 mm.

$$\underset{\text{(III.)}}{CO_2Et\cdot CMe<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}} \longrightarrow \underset{\text{(IV.)}}{CO_2Et\cdot CMe<\begin{matrix}CH_2\cdot C(OH)\cdot CMe_2\cdot CO_2Et\\ CH_2\cdot CH_2\end{matrix}}.$$

This ester is heated with phosphorus tribromide, when water is eliminated and *ethyl dehydrohomofenchonate*, b. p. 152—153°/12 mm., produced. This yields a mixture of *acids*, $C_{11}H_{16}O_4$, on hydrolysis, minute needles, m. p. 176—177°, and compact crystals, m. p. 110—111°. The ester is reduced by means of hydrogen in the presence of spongy platinum and acetic acid to *ethyl homofenchonate*, b. p. 150—155°/13 mm. *Homofenchonic acid*,

$$CO_2H\cdot CMe<\begin{matrix}CH_2\cdot CH\cdot CMe_2\cdot CO_2H\\ CH_2\cdot CH_2\end{matrix},$$

separates from water in minute crystals, m. p. 167—168°.

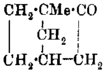
Ethyl 1-methyl*cyclo*pentan-3-one-1-carboxylate (III) is condensed with ethyl bromoacetate in the presence of zinc and a trace of iodine to form a mixture of the two esters, V and VI.

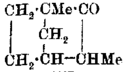
$$\underset{\text{(V.)}}{CO_2Et\cdot CMe<\begin{matrix}CH_2\cdot C(OH)\cdot CH_2\cdot CO_2Et\\ CH_2\cdot CH_2\end{matrix}}$$

$$\underset{\text{(VI.)}}{CO_2Et\cdot CMe<\begin{matrix}CH_2\cdot C{:}CH\cdot CO_2Et\\ CH_2\cdot CH_2\end{matrix}}.$$

The mixture is completely dehydrated by shaking with phosphorus tribromide in chloroform, and then the *ester* (VI), m. p. 148—152°/15 mm., is reduced as above to *ethyl methylnorhomocamphorate*, b. p. 147—149°/14 mm. The free *acid* (3-*carboxymethyl*-1-*methyl*cyclo*pentane*-1-*carboxylic acid*) has m. p. 116—118°, and its lead salt breaks down on distillation in a current of carbon dioxide into *methyl*nor*camphor* (VII), which is a mobile oil, b. p. 60—62°/15 mm., with camphor-like odour (*semicarbazone*, m. p. 210—211°). This is methylated by means of sodamide and methyl

iodide, and so converted into a mixture of fenchosantenone (VIII) and *dl*-fenchone.


(VII.)


(VIII.)

These can be separated by reason of the fact that fenchone does not readily form a semicarbazone, the method being the one used by Wallach to separate camphor and fenchone (A., 1907, i, 616). Fenchosantenone *semicarbazone* forms glistening needles, m. p. 208—209°, and the *oxime* has m. p. 98—99°. The *dl*-fenchone obtained had b. p. 72—73°/12 mm., and its oxime had the correct m. p., 158—159°.

It is suggested that the same general plan might be followed in the synthesis of camphor and *iso*fenchone. J. C. W.

Synthesis by means of Sodamide. Preparation of the Mono- and Di-methylcamphors, of Dimethylcampholamide, and of Dimethylcampholic Acid. A. HALLER and ED. BAUER (*Ann. Chim.*, 1917, [ix], **8**, 117—145).—When camphor (1 mol.) is boiled in anhydrous benzene with one-quarter of its weight of sodamide until all action ceases, and then methyl iodide (1 mol.) is gradually added, and the whole process repeated, a mixture of methylcamphor and dimethylcamphor is obtained, which can be separated by converting the methylcamphor into its oxime and fractionally distilling the mixture. *Dimethylcamphor* is obtained as a colourless, mobile liquid, b. p. 106°/11 mm., D_4^{25} 0·94708, n_α 1·46940, n_D 1·47187, n_β 1·47793, n_γ 1·48289, $[\alpha]_D^{25}$ +97°50′, and in alcoholic solution +92°27′. By the action of sodium in absolute alcohol, it is converted into a mixture of *a-dimethylcamphol*, m. p. 56—57°, $[\alpha]_D^{22}$ +55°4′ (in alcohol) and $[\alpha]_D^{20}$ +60°4′ (in benzene), and *β-dimethylcamphol*, which is not obtained entirely free from its stereoisomeride. The mixed camphols give a *phenylurethane*, m. p. 111·5—112°, $[\alpha]_D^{21}$ +29·5° (in alcohol). With sodamide in benzene solution, dimethylcamphor yields *dimethylcampholamide*, m. p. 72—73°, b. p. 179—180°/14 mm., $[\alpha]_D^{22}$ 70·8°, which by the action of sodium nitrite in the presence of sulphuric acid is converted into *dimethylcampholic acid*, m. p. 73—74°, $[\alpha]_D^{21}$ 47·4° (in alcohol).

The methylcamphoroxime as isolated has m. p. 60°, b. p. 134—135°/11 mm., $[\alpha]_D^{22}$ +23·15° (compare Glover, T., 1908, **93**, 1285), and is shown to be a mixture of an active and an inactive form. With phenylcarbimide it gives two isomeric *a-methylcamphorcarbanilidoximes*, the one crystallising in prisms, m. p. 112—113°, $[\alpha]_D^{22}$ +24·8° (in alcohol), and the other in needles, m. p. 113°, and inactive. Methylcamphoroxime when boiled with hydrochloric acid yields *a-methyl-a-campholenonitrile*, b. p. 105°/15 mm., $[\alpha]_D^{23}$ 53·9° (in alcohol), which when boiled with

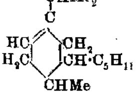
alcoholic potassium hydroxide gives *a-methylcampholenamide*, m. p. 91—92°, crystallising with $1H_2O$, and quite inactive, and if the hydrolysis is carried further, *methylcampholenic acid*, m. p. 30°, b. p. 153°/20 mm., which is also inactive, is obtained.

W. G.

Constituents of Essential Oils. Elemol, $C_{15}H_{26}O$. F. W. SEMMLER and FUTUNG LIAO (*Ber.*, 1917, **50**, 1286—1291. Compare A., 1916, i, 492).—A further account of this unicyclic sesquiterpene alcohol.

Pure tetrahydroelemol, obtained from the purest elemol or from its benzoate, has m. p. 35·5°, b. p. 138—142°/13 mm., D^{20} 0·9080, n_D 1·4807, α_D −2°. It forms a *benzoate*, b. p. 210—215°/13 mm., D^{20} 0·9927, n_D 1·5092, α_D −8°, and an *acetate*, b. p. 152—155°/12 mm., D^{20} 0·9304, n_D 1·4641, α_D +2°. From the purified oil, a specimen of tetrahydroelemene with b. p. 118—120°/12 mm., D^{20} 0·8576, n_D 1·4760, α_D −15·2°, was obtained by treatment with formic acid.

In order to elucidate the constitution of elemol, the ozonisation of tetrahydroelemene, as the most suitable material, has been investigated. The important products, after decomposing the *ozonides*, are a *keto-aldehyde*, $C_{15}H_{28}O_2$, b. p. 140—170°/10 mm., which reacts with semicarbazide to give a complicated mixture, and the corresponding *ketonic acid*, $C_{15}H_{28}O_3$, b. p. 180—205°/10 mm., which forms a *methyl* ester, b. p. 165—170°/10 mm. A considerable yield of the acid is obtained if the ozonisation is prolonged until the yellow colour which develops at first disappears again. The keto-acid gives a *dicarboxylic acid*, $C_{12}H_{22}O_4$, b. p. 180—205°/10 mm., when oxidised by a hypobromite solution, which indicates the presence of an *iso*propyl group. Tetrahydroelemene may therefore have the annexed formula, but the position of the side-chain is not yet determined.



Crude elemol contains small quantities of a more volatile, denser oil, b. p. 135—145°/10 mm., D^{20} 0·9670, n_D 1·5171, α_D −3·6°, which may be a *phenolic ether*,

$$C_6H_2(OMe)_3{\cdot}CH_2{\cdot}CH{:}CH_2$$

or $C_6H_2(OMe)_3{\cdot}CH_2{\cdot}CH{:}CHMe$, for it may be oxidised to an *acid*, $C_6H_2(OMe)_3{\cdot}CH_2{\cdot}CO_2H$, m. p. 185—186°.

J. C. W.

The Colloidal Nature of Colophony. I. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 115—124).—The nature of colophony is discussed in reference to the various products which are obtained by the action of acids on its solutions in alkalis. The chief substance is γ-pinic acid, m. p. 75—76°, which contains a maximum amount of combined water in a colloidal form. By the action of dehydrating agents, sylvic acid and "Malysäure" are formed as intermediate products, the final product of the dehydration process

being γ-abietic acid, m. p. 161—163°. These substances form a series which offers some resemblance to the silicic acids commencing with colloidal silicic acid and ending with silica.

Hydrocarbons and ethers behave similarly to water, and enter into combination with colophony in colloidal form. The solid colloidal solutions which are thereby formed represent a new and distinct type from the point of view of the colloid chemist, and commercial colophony is to be regarded as belonging to this group.

H. M. D.

Bixin. A. Heiduschka and A. Panzer (*Ber.*, 1917, **50**, 1525—1526).—A reply to Herzig and Faltis (A., 1917, i, 577) maintaining the probability of the formula $C_{25}H_{30}O_4$ for bixin.

D. F. T.

3 : 4-Di-*p*-nitrotetraphenylfuran. Arthur Gordon Francis (T., 1917, **111**, 1039—1043).—When *p*-nitroacetylbenzoin and *p*-nitrobenzoylbenzoin are hydrolysed by means of alcoholic hydrogen chloride, they yield *p*-nitrobenzil and 3:4-*di*-p-*nitrotetraphenylfuran*. The reaction is supposed to proceed as follows. First, the acyl compound is hydrolysed to *p*-nitrobenzoin; two molecules of this condense together, and the product is reduced to dinitrobidesyl at the expense of a third molecule, which is oxidised to p-nitrobenzil, thus:

$$3NO_2\cdot C_6H_4\cdot CHBz\cdot OH = NO_2\cdot C_6H_4\cdot CHBz\cdot CHBz\cdot C_6H_4\cdot NO_2 + NO_2\cdot C_6H_4\cdot COBz,$$

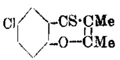
and, finally, the dinitrobidesyl suffers loss of water and changes into the furan, $O<\begin{matrix}CPh:C\cdot C_6H_4\cdot NO_2\\ CPh:C\cdot C_6H_4\cdot NO_2\end{matrix}$. The intermediate products have not been isolated, but analogous compounds in the case of benzoin itself are well known.

For experimental details, see the original. J. C. W.

Formation of Halogenated Chromones [γ-Benzopyrones]. H. Simonis and Hans Schuhmann (*Ber.*, 1917, **50**, 1142—1149).—It was recently shown that, by vigorous methods, bromine can be introduced into the methyl groups of 2:3-dimethylchromone, but that the benzene nucleus is only affected under extreme conditions (A., 1917, i, 408). Chromones containing halogens in the benzene nucleus can, however, be obtained readily by the condensation of halogenophenols with alkylacetoacetic esters under the influence of phosphoric oxide (compare A., 1913, i, 890). On the other hand, halogen atoms in the ester component hinder the condensation with phenols, and chromones substituted in the pyrone nucleus cannot be obtained by this method.

p-Chlorophenol and ethyl methylacetoacetate yield 6-*chloro*-2 : 3-*dimethyl*-γ-*benzopyrone*, in long needles, m. p. 107°. This forms an *oxime*, m. p. 202°, reacts with phosphorus pentasulphide at

120° to give 6-*chloro*-2:3-*dimethyl*-γ-*benzothiopyrone* (annexed formula), red needles, m. p. 142·5°, and is hydrolysed by boiling, dilute sodium hydroxide to 5-chlorosalicylic acid. 6-*Chloro*-2-*methyl*-3-*ethyl*-γ-*benzopyrone*, needles, m. p. 109°, from ethyl ethylacetoacetate, forms an *oxime*, m. p. 165·5°, and a *compound* with $1HgCl_2$, which crystallises in needles, often an inch long.



p-Bromophenol gives rise to 6-*bromo*-2:3-*dimethyl*-γ-*benzopyrone*, which crystallises in very long prisms, m. p. 111—112°, and 6-*bromo*-2-*methyl*-3-*ethyl*-γ-*benzopyrone*, long needles, m. p. 190°.

o-Chlorophenol yields 8-*chloro*-2:3-*dimethyl*-γ-*benzopyrone*, pale yellow leaflets, m. p. 108°, and 8-*chloro*-2-*methyl*-3-*ethyl*-γ-*benzopyrone*, long spikes, m. p. 85°, which forms a *compound* with $1HgCl_2$, pale yellow columns, m. p. 134°.

o-Bromophenol gives 8-*bromo*-2 : 3-*dimethyl*-γ-*benzopyrone*, needles, m. p. 108°, which yields 3-bromosalicylic acid, m. p 183—184°, on hydrolysis, and 8-*bromo*-2-*methyl*-3-*ethyl*-γ-*benzopyrone*, prisms, m. p. 94°.

m-Halogenophenols can theoretically give 5- and 7-halogeno-derivatives. As usual, their constitutions are best revealed by identifying the halogeno-salicyclic acids or other products which they yield on hydrolysis. *m*-Chlorophenol and ethyl dimethylacetoacetate give a mixture from which 7-*chloro*-2:3-*dimethyl*-γ-*benzopyrone*, m. p. 155°, can be isolated; this yields 4-chlorosalicylic acid on hydrolysis. *m*-Bromophenol, on one occasion, gave 5-*bromo*-2:3-*dimethyl*-γ-*benzopyrone*, m. p. 163°, only, but usually the 7-*bromo*-compound, m. p. 108—110°, is formed as well. It has already been shown that the former yields 6-bromo-2-hydroxyphenyl ethyl ketone on hydrolysis, and the latter 4-bromosalicylic acid (A., 1917, i, 580). Individual compounds are usually given by ethyl ethylacetoacetate, but their constitutions have not been determined. 5- or 7-*Chloro*-2-*methyl*-3-*ethyl*-γ-*benzopyrone* has m. p. 133°, and the 5- or 7-*bromo*-compound has m. p. 137°.

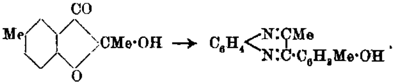
2:4-Dihalogenophenols react to form the 6:8-dihalogenochromones, but the condensation does not take place so readily. 6:8-*Dichloro*-2:3-*dimethyl*-γ-*benzopyrone* has m. p. 141°, the 6:8-*dibromo*-compound has m. p. 128·5°, and 6:8-*dichloro*-2-*methyl*-3-*ethyl*-γ-*benzopyrone* has m. p. 105°. J. C. W.

Further Investigations on the Formation and Opening of the Coumaranone Ring. K. von Auwers and W. Müller (*Ber.*, 1917, **50**, 1149—1177. Compare A., 1914, i, 981, 1136; 1915, i, 440; 1916, i, 496; 1917, i, 277).—It has been shown that 1:4-dimethylcoumaran-2-one readily changes into 4-acetoxy-*m*-toluic acid on exposure to the air. The rupture of the heterocyclic system between positions 1 and 2 during auto-oxidation is not exhibited to such a remarkable degree by other alkylcoumaranones, and no conclusions as to the connexion between structure and reactivity in this sense can safely be drawn.

The coumaranone ring can often be opened, however, between the oxygen atom and carbon atom 1, by means of the ketone reagents, semicarbazide (A., 1915, i, 440), hydroxylamine, *o*-phenylenediamine, and some phenylhydrazines. The behaviour of various coumaranones towards these reagents has therefore been examined, in order to determine, if possible, the influence of substituents on the stability of the ring. It is found, as before, that substituents in the benzene nucleus in the ortho- or para-positions with regard to the oxygen atom generally tend to weaken the ring, whilst meta-substituents have a stabilising effect.

Conversely, the ease with which *o*-α-halogenoacylphenols undergo ring closure to coumaranones when treated with alkali hydroxides has been examined. Extreme cases are represented by 6-chloroacetyl-5-*m*-xylenol, which changes with the greatest ease into 3:5-dimethylcoumaranone, and *m*-α-bromo*iso*butyryl-*p*-cresol, which yields either *m*-α-hydroxy*iso*butyryl-*p*-cresol or 3:6-dimethyl-1:4-benzopyrone, but no coumaranone at all. Many intermediate cases are now described in which both reactions take place, but it is evident that meta-substituents with regard to the hydroxyl group favour the formation of coumaranones, and that methoxyl is more active in this respect than methyl.

1:4-DIMETHYLCOUMARANONE SERIES.—1:4-Dimethylcoumaranone does not react with *o*-phenylenediamine, but 1-hydroxy-1:4-dimethylcoumaran-2-one condenses with this agent in boiling acetic acid to form *2-4′-hydroxy-*m*-tolyl-3-methylquinoxaline*, thus:



This compound crystallises in large, glistening prisms, m. p. 194—195°, and reacts with methyl sulphate to form a *methyl ether*, silky needles, m. p. 96—97°, which may also be prepared by condensing *o*-phenylenediamine with 4-methoxy-*m*-tolyl methyl diketone, $OMe·C_6H_3Me·CO·COMe$ (A., 1915, i, 440).

3-α-Chloropropionyl-*p*-cresol dissolves in 2*N*-sodium hydroxide with golden-yellow colour, giving chiefly the coumaranone derivative, but also some α-hydroxypropionylcresol. These were not isolated as such, but converted into methyl ethers by means of methyl sulphate, and then separated by distillation. *2-Methoxy-1:4-dimethylcoumarone*, $C_6H_3Me<\genfrac{}{}{0pt}{}{C(OMe)}{O}>CMe$, distils, first, as a colourless, pleasant-smelling oil, b. p. 126—126·5°/19 mm.; D_4^{20} 1·081, n_D^{20} 1·5451, $E\Sigma_a$ +0·77, $E\Sigma_D$ +0·85, $E\Sigma_\beta - \Sigma_a$ +55%, $E\Sigma_\gamma - \Sigma_a$ +64% (average values). The same compound is obtained by shaking an alkaline solution of 1:4-dimethylcoumaranone with methyl sulphate. The liquid with higher b. p. is *m-lactyl-p-methoxytoluene*, $OMe·C_6H_3Me·CO·CHMe·OH$, and is a pale yellow oil, b. p. 154—156°/16 mm., D^{20} 1·099, n^{20} 1·5250, EΣ +0·81

$E\Sigma_D + 0{\cdot}85$, $E\Sigma_\beta - \Sigma_\alpha + 44\%$. The same oil was synthesised as follows: *m*-propionyl-*p*-methoxytoluene is brominated, the *m*-α-bromopropionyl compound (b. p. 161—163°/14 mm.) is boiled with potassium acetate in dry alcohol, and the m-*α-acetoxypropionyl*-p-*methoxytoluene* (glassy needles, m. p. 70—71°) is hydrolysed.

4-METHYL-1-ETHYLCOUMARANONE SERIES.—3-*α-Chlorobutyryl*-p-*cresol* is prepared by the condensation of α-bromobutyryl bromide with *p*-cresol methyl ether under the influence of aluminium chloride. It crystallises in stout, glassy prisms, m. p. 61—62°, b. p. 159—160°/12 mm., and condenses, under the influence of sodium acetate or hydroxide, to 4-*methyl*-1-*ethylcoumaran*-2-*one*. This crystallises in long, flat, glassy prisms, m. p. 41°, b. p. 140—142°/14 mm., and has a sweet odour. The *acetate* (of the enolic form) is a highly refractive oil, b. p. 160—161°/13 mm., which is immediately hydrolysed by alkali hydroxides. It behaves like 1:4-dimethylcoumaranone towards semicarbazide, forming a normal *semicarbazone*, $C_{12}H_{15}O_2N_3$, glassy needles, m. p. 195°, which is insoluble in sodium hydroxide, and then suffering rupture of the ring, with the production of the *compound*,

$$OH{\cdot}C_6H_3Me{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CHEt{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

or the true disemicarbazone,

$$OH{\cdot}C_6H_3Me{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CEt{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

This is soluble in alkali hydroxides, forms slender needles, m. p. 223—224°, and is hydrolysed by hydrochloric acid to 1-*hydroxy*-4-*methyl*-1-*ethylcoumaran*-2-*one*, which crystallises in glistening needles, m. p. 95—96°. The latter compound is more easily prepared by the action of sodium carbonate on 1-*bromo*-4-*methyl*-1-*ethylcoumaran*-2-*one*, which is obtained in silky needles, m. p. 44—45°, by brominating 4-methyl-1-ethylcoumaranone.

4-METHYL-1-*iso*PROPYLCOUMARANONE SERIES.—3-*α-Chloro*iso*valeryl*-p-*cresol*, from α-bromo*iso*valeryl bromide, *p*-cresol methyl ether, and aluminium chloride, crystallises in glistening, yellow needles, m. p. 75—76°, and is readily converted, as above, into 4-*methyl*-1-iso*propylcoumaran*-2-*one*. This crystallises in long prisms, m. p. 25—26·5°, b. p. 147—148°/16 mm., and forms an *acetate*, b. p. 162—163·5°/13 mm. It is very stable towards semicarbazide, and even the *semicarbazone*, m. p. 170—171°, is only produced in a small yield. The *oxime*, glistening, slender needles, m. p. 142—143°, is more readily formed, but an excess of hydroxylamine does not bring about rupture of the ring. 1-*Bromo*-4-*methyl*-1-iso*propylcoumaran*-2-*one*, silky needles, m. p. 65·5—66·5°, is obtained by direct bromination, and converted, as above, into the 1-*hydroxy*-compound, felted needles, m. p. 118—119°. This is stable towards semicarbazide, but reacts with *o*-phenylenediamine to give 2-4′-*hydroxy*-m-*tolyl*-3-iso*propylquinoxaline*,

$$C_6H_4<\begin{matrix}N{:}CPr^\beta \\ N{:}C{\cdot}C_6H_3Me{\cdot}OH\end{matrix}$$

m. p. 161—162°.

1:3:5-TRIMETHYLCOUMARANONE SERIES.—The methyl ether of *s.-m*-xylenol and α-bromopropionyl bromide condense together, under the influence of aluminium chloride, to give a mixture containing 60—70% of the coumaranone directly. Any of the normal chloro-ketone in the mixture is readily transformed into the coumaranone by means of sodium hydroxide. 1:3:5-*Trimethylcoumaran-2-one* forms large, transparent crystals, m. p. 25—27°, b. p. 142·5—143°/14 mm., yields an *acetate*, long, glassy needles, m. p. 60—61°, b. p. 163·5—164/14 mm., and gives a very poor yield of a *semicarbazone*, m. p. 231—232°. 1-*Hydroxy*-1:3:5-*trimethylcoumaran-2-one* is obtained through the 1-bromo-derivative, in glistening needles, m. p. 115—117°.

5-METHOXY-1-METHYLCOUMARANONE SERIES.—Resorcinol dimethyl ether and α-bromopropionyl bromide are condensed together, under the influence of aluminium chloride, to form 6-α-*chloropropionyl*-3-*methoxyphenol*, stout, yellow, glassy prisms, m. p. 84—85°, and this is converted into 5-*methoxy*-1-*methylcoumaran-2-one*, which crystallises in long, glistening needles, m. p. 60—61°. Semicarbazide reacts with this ketone to form the *semicarbazone*, m. p. 194—195°, and after a time the *disemicarbazone*, $C_{12}H_{16}O_4N_6$, m. p. 235—236°, of the opened, unicyclic compound. 1-*Bromo*-5-*methoxy*-1-*methylcoumaran-2-one* forms bundles of silky needles, m. p. 74—75°, and the 1-*hydroxy*-compound, which may be obtained from the bromo-derivative, or by boiling the above disemicarbazone with dilute hydrochloric acid, crystallises in glistening prisms, m. p. 115—116°.

4-METHOXY-1-METHYLCOUMARANONE SERIES.—Quinol dimethyl ether and α-bromopropionyl bromide give rise to 4-*methoxy*-2-α-*chloropropionylphenol*, which crystallises in deep yellow needles, m. p. 47—49°, b. p. 181—183°/13 mm., and may be converted into 2-*propionyl*-4-*methoxyphenol* (long, glassy needles, m. p. 47—49°, b. p. 158—160°/19 mm.) by the action of zinc and acetic acid. The chloroketone reacts with sodium acetate to give a yellow oil which is apparently a mixture of 4-methoxy-1-methylcoumaranone and unicyclic hydroxy-ketone. The mixture reacts most readily with semicarbazide to form the *disemicarbazone*,

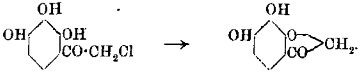
$$OMe\cdot C_6H_3(OH)\cdot C{<}^{N\cdot NH\cdot CO\cdot NH_2}_{CMe:N\cdot NH\cdot CO\cdot NH_2},$$

m. p. 207—208°. No trace of a coumaranone semicarbazone can be found. The crude chloroketone behaves similarly with sodium hydroxide, and in this case it is possible to methylate the product, and so to isolate 2:4-*dimethoxy*-1-*methylcoumarone*,

$$OMe\cdot C_6H_3{<}^{C(OMe)}_{O}{>}CMe,$$

b. p. 150—150·5°/15 mm., D_4^{20} 1·444, n_D^{20} 1·5520, $E\Sigma_\alpha$ +0·94°, $E\Sigma_D$ +1·02, $E\Sigma_\beta - \Sigma_\alpha$ + 65%, $E\Sigma_\gamma - \Sigma_\alpha$ + 77%, and 2-*lactyl*-1:4-*dimethoxybenzene*, $C_6H_3(OMe)_2\cdot CO\cdot CHMe\cdot OH$, b. p. 172—175°/15 mm., D_4^{20} 1·142, n_D^{20} 1·5323, $E\Sigma_\alpha$ +1·26, $E\Sigma_D$ +1·31, $E\Sigma_\beta - \Sigma_\alpha$ + 60%. J. C. W.

Hydroxycoumaranones. ADOLF SONN (*Ber.*, 1917, **50**, 1262—1270).—The most suitable method for the preparation of hydroxycoumaranones seems to be to bring about internal condensation in *o*-chloroacetyl derivatives of the polyhydric phenols, as, for example, in the formation of 5:6-dihydroxycoumaranone ("anhydroglycogallol") from 6-chloroacetylpyrogallol,



The usual methods for the preparation of the chloroacetyl derivatives are of very limited application, and leave much to be desired, but they can be obtained most readily from chloroacetonitrile and the phenols by Hoesch's new ketone synthesis (A., 1915, i, 820).

An ethereal solution of phloroglucinol and chloroacetonitrile is saturated with hydrogen chloride, when the hydrochloride of the keto-imide, $C_6H_2(OH)_3{\cdot}C(CH_2Cl){:}NH,HCl$, is precipitated. This is hydrolysed, as usual, by boiling with water, but the chloroacetylphloroglucinol almost entirely changes into the coumaranone during the same operation. The condensation is completed by adding a little chalk or potassium acetate to the water. 3:5-*Dihydroxycoumaranone* forms stout, glassy tablets, m. p. 250° (decomp.), and yields a *diacetate*, glistening, hexagonal prisms, m. p. 122°, and a 1-*anisylidene* compound, stellate bundles of orange-yellow needles, m. p. 224—225°.

An excellent yield of 6-*chloroacetylresorcinol* can be obtained by the same method. The ketone crystallises in stout prisms or thick bundles of slender needles, m. p. 131°, and reacts with diazomethane to form 3-methoxy-6-chloroacetylphenol (ω-chloro-2-hydroxy-4-methoxyacetophenone; Auwers and Pohl, A., 1914, i, 981), from which 5-methoxycoumaranone (*ibid.*) is readily obtained. It is also converted into 5-*hydroxycoumaranone* (Brüll and Friedländer's *m*-hydroxyketocoumaran, A., 1897, i, 221) by boiling with alcohol and potassium acetate. This compound crystallises in pearly leaflets, m. p. 242°, and reacts with acetic anhydride to form a mono-acetate, pearly scales, m. p. 79° (*ibid.*), and a *diacetyl* derivative, stout crystals, m. p. 157—159°.

J. C. W.

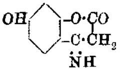
4-Hydroxycoumarins. ADOLF SONN (*Ber.*, 1917, **50**, 1292—1305).—Some applications of Hoesch's method (A., 1915, i, 820; 1917, i, 342) to the production of 4-hydroxycoumarins are described.

Phloroglucinol and malononitrile are condensed together by means of hydrogen chloride, and the intermediate imide hydrochloride is boiled with water, when *o*-*cyanoacetylphloroglucinol*, $CN{\cdot}CH_2{\cdot}CO{\cdot}C_6H_2(OH)_3$, m. p. 260° (decomp.), together with 2:4:6:2′:4′:6′-*hexahydroxydibenzoylmethane*, elongated tablets, which blacken at 300°, are produced. The cyanoacetylphloroglucinol changes into 4:5:7-trihydroxycoumarin (below) when boiled with dilute acids. Resorcinol behaves in a similar manner,

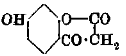
yielding 6-cyanoacetylresorcinol, nodules of needles, m. p. 270—272° (decomp.), which changes into 4 : 7-dihydroxycoumarin (below) on hydrolysis.

Instead of using malononitrile in the above syntheses, cyanoacetic acid may be employed. This gives stable 4-*imino-compounds* of the coumarins, which can be converted into acetyl and methoxyl derivatives or hydrolysed by means of 50% sulphuric acid to the 4-hydroxycoumarins.

Resorcinol, cyanoacetic acid, and zinc chloride are mixed in ether and saturated with hydrogen chloride, when *4-imino-7-hydroxy-3 : 4-dihydro-1 : 2-benzopyrone* (annexed formula) is obtained.



This crystallises from about 65% acetic acid, has m. p. 340° (decomp.), dissolves in dilute potassium hydroxide with bluish-violet fluorescence, and can be recovered unchanged, and forms a characteristic *diacetyl* compound, glistening needles, m. p. 251°, which changes into a *monoacetyl* derivative (hydroxyl group open ?), m. p. 295° (decomp.), when dissolved in dilute alkali hydroxide. The compound may also be converted into the 7-*methoxy*-derivative by means of methyl sulphate; this crystallises from acetic acid in heavy, glistening, hexagonal columns, m. p. 300° (decomp.), and forms an *acetyl* compound, m. p. 295° (decomp.). The imide is hydrolysed, as mentioned above, to *4 : 7-dihydroxycoumarin* (*7-hydroxy-4-keto-3 : 4-dihydro-1 : 2-benzopyrone*) (annexed formula).



This crystallises from water in long, silky needles, $2H_2O$, m. p. 265° (decomp.), and forms a *diacetate*, which changes into the 7-*acetyl* compound, m. p. 223°, when distilled with steam. It also yields *4 : 7-dimethoxycoumarin*, long, slender needles, m. p. 156°, and the 7-*methoxy*-derivative,

$$OMe\cdot C_6H_3{<}^{O-CO}_{CO\cdot CH_2},$$

long, pliable needles, m. p. 256° (decomp.), when treated with methyl sulphate; the latter is soluble in alkali hydroxides. The compound also condenses with aldehydes under the influence of hydrochloric acid, and forms a 3-oximino-derivative.

Phloroglucinol and cyanoacetic acid react in the presence of hydrogen chloride to form *4-imino-5 : 7-dihydroxy-3 : 4-dihydro-1 : 2-benzopyrone*, which crystallises in prismatic needles, m. p. above 300° (decomp.). The compound is sparingly soluble in hot water, but a much more soluble modification is obtained if ethyl cyanoacetate is used instead of the free acid. Both forms yield the same *triacetyl* derivative, long, very thin needles, m. p. 197°, which changes into a *diacetyl* compound, m. p. 300° (decomp.), when dissolved in dilute sodium hydroxide. The keto-imide also forms a 5 : 7-*dimethoxy*-compound, stout, double pyramids, m. p. 260° (*acetyl* derivative, m. p. 213°), and may be hydrolysed by dilute sulphuric acid to 4 : 5 : 7-trihydroxycoumarin (5 : 7-dihydr-

oxy-4-keto-3 : 4-dihydro-1 : 2-benzopyrone). This compound has hitherto been obtained by the hydrolysis of Jerdan's lactone (compare Leuchs and Sperling, A., 1915, i, 141), but the present method is much more direct. The anhydrous ketone sinters at 210° and has m. p. above 300° (decomp.). It forms a *triacetate*, m. p. 155—156°, and a *diacetate*, m. p. 210—211°, and a 3-*anisylidene* compound, $C_6H_2(OH)_2<\begin{matrix}O-CO\\CO\cdot C:CH\cdot C_6H_4\cdot OMe\end{matrix}$, in delicate, orange-yellow needles, m. p. 256° (decomp.).

Jerdan's lactone, ethyl 4 : 5 : 7-trihydroxycoumarin-8(or 6)-carboxylate (A., 1917, i, 277), forms a *triacetate*, in hard, stout, hexagonal prisms, m. p. 146—147°, which change into Leuchs and Sperling's diacetate, m. p. 196—197°, when treated with cold alkali hydroxide or boiled with water. It also reacts with nitrous acid to give a 3-*oximino*-compound, pale greenish-grey, elongated tablets, m. p. 157° (decomp.). J. C. W.

***N*-Methylconiine.** J. von Braun (*Ber.*, 1917, **50**, 1477).—The methylconiine, $[\alpha]_D$ +35·66°, obtained earlier by the author from hemlock (A., 1905, i, 811) was in reality a mixture of *d*- and *l*-methylconiine, the former predominating, and the salts then described were those of the *dl*-base (see also Hess and Eichel, this vol., i, 34). D. F. T.

The Alkaloids of the Pomegranate Tree. III. Constitution of Pelletierine. Kurt Hess and Annaliese Eichel (*Ber.*, 1917, **50**, 1192—1199. Compare A., 1917, i, 349).—Further researches on pelletierine have revealed the interesting fact that the alkaloid is the aldehyde of coniine, or β-2-*piperidylpropaldehyde*.

Pelletierine yields an *oxime*, b. p. 173°/21 mm., which occurs apparently in two geometric forms, m. p. 96—97° (from light petroleum) and m. p. 80° (from ether), and gives a *picrate*, m. p. 179—180°. When the oxime is treated with phosphorus pentachloride, both dissolved in warm phenetole, it changes into the corresponding *nitrile*, which is a stable, mobile oil, b. p. 104—106°/15 mm., with a pungent, menthol-like odour, and forms a *picrate*, in long needles, m. p. 175—176°. The nitrile may be hydrolysed to the acid and this converted into the ester, which is identical with Löffler and Kaim's ethyl β-2-piperidylpropionate (A., 1909, i, 179). The acid has not yet been obtained by oxidising pelletierine.

Pelletierine *hydrazone* is a limpid syrup, b. p. 150°/20 mm., which is reduced to racemic coniine by heating with sodium ethoxide solution in a sealed tube at 156—170°. The identity of the product is fully established.

Although a secondary base, pelletierine does not react with nitrous acid. This is obviously due to some influence of the aldehyde group on the imino-group. J. C. W.

The Alkaloids of the Pomegranate Tree. IV. A Scheme for the Isolation of the Pure Pelletierine Alkaloids. Determination of the Constitution of Methyl*iso*pelletierine ("Methylpelletierine." "*iso*Methylpelletierine"). Transformation of Conhydrine into Methyl*iso*pelletierine. Constitution of Conhydrine. KURT HESS and ANNALIESE EICHEL (*Ber.*, 1917, **50**, 1386—1407).—In the new investigations of the pelletierine alkaloids, the authors have not encountered optically active bases, and are inclined to doubt whether the active "pelletierine" and "methylpelletierine" described by Tanret were really pure. They have therefore adopted the name "pelletierine" for the inactive base which Tanret designated *iso*pelletierine, and have also shown that Tanret's methylpelletierine and Piccinini's *iso*methylpelletierine are identical. The latter base is not really a methylated pelletierine, but a methyl derivative of an unknown *iso*pelletierine, and therefore the new name methyl*iso*pelletierine is proposed.

Methyl*iso*pelletierine is already known to be a tertiary base with a carbonyl group, and the formula $C_9H_{17}ON$ is well established. It is possible to convert its hydrazone into 1-methylconiine, as pelletierine was transformed into *dl*-coniine (preceding abstract). It may therefore be one of the three bases represented thus:

$$CH_2{<}{CH_2-CH_2 \atop CH_2\cdot NMe}{>}CH-\underset{(A)}{CH_2\cdot CH_2\cdot CHO} \text{ or } \underset{(B)}{-CH_2\cdot COMe} \text{ or } \underset{(C)}{-COEt}.$$

It is not identical with *A*, which is methylpelletierine (A., 1917, i, 350), or with *B*, which is α-1-methylpiperidyl-2-propan-β-one (*ibid.*, 352), and therefore it can only be the compound *C*.

It is an interesting fact that pelletierine and methyl*iso*pelletierine are so closely connected with coniine and 1-methylconiine, two of the hemlock alkaloids. Conhydrine is also nearly related to methyl*iso*pelletierine. Its structure had not been definitely established hitherto, but it can be converted into methyl*iso*pelletierine, and is thus revealed as α-2-piperidylpropyl alcohol.

Attention is directed again to the fact that no optically active modifications of these bases have been found in the pomegranate root. Whilst animals almost exclusively synthesise one active isomeride (except in the case of lactic acid fermentation), the pomegranate, at any rate, produces both forms or is able to bring about racemisation.

After many attempts, it has been found that the best way to separate pelletierine and methyl*iso*pelletierine is to treat the mixture with ethyl chloroformate, when the former, as a secondary base, yields a urethane, whilst the latter, as a tertiary base, remains unchanged, and has a much lower b. p. than the urethane. A new scheme for the isolation of the three alkaloids, crystalline ψ-pelletierine, b. p. 145°/vac., pelletierine, b. p. 106°/21 mm., and methyl*iso*pelletierine, b. p. 114—115°/24 mm., from the root-rind of the pomegranate tree, is now described.

The *urethane* from pelletierine, β-1-*carbethoxypiperidyl-2-prop-*

aldehyde, is a limpid, slightly viscous oil, b. p. 173—174°/20—21 mm., and is readily hydrolysed to pelletierine by heating with concentrated hydrochloric acid at 125—130°.

Methyl*iso*pelletierine *hydrobromide* crystallises in very long needles, m. p. 151—152°, and depresses the m. p. of 1-methylpelletierine hydrobromide. The *hydrazone* is a stable, limpid oil, b. p. 154—155°/29 mm., which yields *dl*-1-methylconiine when heated with sodium ethoxide solution at 150—170°. The identity of the base is fully established by means of the usual salts. Although *d*-coniine is rendered almost inactive by heating with barium hydroxide solution and alcohol at 180—230°, it yields a highly active 1-methylconiine when heated with formaldehyde and formic acid at 125—130°. Consequently, a specimen of *dl*-methylconiine was obtained for comparative purposes by methylating the *dl*-coniine derived from pelletierine.

Conhydrine, $[\alpha]_D^{20}$ + 7·12°, is also methylated by the formaldehyde-formic acid method. 1-*Methylconhydrine* (*α-1-methylpiperidyl-2-propyl alcohol*) has b. p. 102—103°/19 mm., and the *sulphate* has $[\alpha]_D^{21}$ – 20·9°, in water. When oxidised by chromic acid, it loses the methyl group in addition, and gives *α-2-piperidylpropan-α-one* (*2-piperidyl ethyl ketone*), b. p. 94°/18 mm.; the *sulphate* has $[\alpha]_D^{23}$ – 7·8°, in water. This behaviour of tertiary 1 : 2-hydroxy-amines may be general, for it has already been observed in the case of α-1-methylpyrrolidyl-2-butyl alcohol (A., 1917, i, 353). 2-Piperidyl ethyl ketone cannot be methylated by the formaldehyde method, but methyl sulphate converts it into 1-*methyl-2-piperidyl-ethyl ketone*, which is identical with methyl*iso*pelletierine.

2-*Piperidylacetone* (*α-2-piperidylpropane-β-one*) has been prepared by the oxidation of α-2-piperidylpropan-β-ol (A., 1916, i, 69); it is a colourless oil, b. p. 108—111°/24 mm., which readily darkens on exposure to air. It yields a *hydrobromide*, m. p. 179°, a *picrate*, m. p. 113—114°, a *semicarbazone hydrochloride*,

$$C_9H_{18}ON_4,HCl,\frac{1}{2}H_2O,$$

m. p. 164—165° (decomp.), and a *urethane*, m. p. 209°. J. C. W.

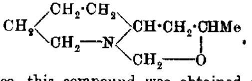
Nicotinic Acid Derivatives. I. E. WINTERSTEIN and A. B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1917, **100**, 170—184).—On the reduction of trigonelline with hydrogen in the presence of platinum-black, a *substance* is produced which in some respects closely resembles arecaidine. It gives a crystalline hydrochloride and platinichlorides and aurichlorides which have the same melting points as those recorded for the corresponding arecaidine compounds. The *N*-methyl derivative, prepared by the action of methyl iodide on the reduction product of trigonelline, yields a platinichloride which is identical in melting point and crystalline form with the corresponding salt prepared from arecaidine. On the other hand, the *aurichloride* (short, stout prisms, m. p. 225—230°) and the *picrate* (needles) of the reduction product differ in crystalline form from the similar compounds derived from arecaidine, whilst the mercury salt melts at 205—208° instead of 174—176°. Moreover, the methyl ester of the reduction product

which should be identical with arecoline, yields a non-crystalline hydrochloride, an *aurichloride*, $C_8H_{13}O_2N,HAuCl_4$, slender needles, m. p. 134—135°, and a *platinichloride*, stout needles, m. p. 192—193°, whilst the corresponding arecoline hydrochloride is a crystalline substance, m. p. 157°, the aurichloride a non-crystalline oil, and the platinichloride crystallises in rhombs, m. p. 176° (decomp.). The authors draw the conclusion that their reduction product from trigonelline is not identical with arecaidine.

When potassium nicotinate is heated at 150° with ethyl iodide and the product shaken with silver chloride, *ethylarecaidine chloride* is formed, needles, m. p. 238°. On reduction, the *chloride* of *ethyltetrahydroarecaidine*, $C_8H_{13}O_2NCl$, is produced, m. p. 230—231°. H. W. B.

Action of Aldehydes on the Hydramines of the Pyrrolidine and Piperidine Series. VI. Action of Formaldehyde on α-2-Piperidylpropan-β-ol. KURT HESS and ANNALIESE EICHEL (*Ber.*, 1917, **50**, 1407—1412. Compare A., 1916, i, 67; 1917, i, 352). —In an earlier paper, it was reported that α-2-piperidylpropan-β-ol is converted into α-1-methyl-2-piperidylpropan-β-one by the action of formaldehyde, but later, when this ketone was prepared by the oxidation of the corresponding secondary alcohol, it was recognised that formaldehyde must have given some other product in the first case. It is now found that the action of formaldehyde on the above secondary alcohol is much more complicated than was imagined.

The base reacts with 40% formaldehyde in the cold to give the *compound* A, b. p. 108—111°/28 mm.; *picrate*, m. p. 160—161°.

(A) 

By a mere chance, this compound was obtained earlier by the action of formaldehyde and hydrochloric acid at above 100°. Under these conditions, it has never been obtained since, reaction taking place according to the equation $C_8H_{17}ON + 2H{\cdot}CHO = C_{10}H_{17}ON + 2H_2O$. The *product* has b. p. 103—107°/23 mm., and forms a *picrate*, m. p. 190°, a *picrolonate*, m. p. 193°, and a *methochloride-aurichloride*, m. p. 98°. It is reconverted into the hydramine by semicarbazide, and is hydrolysed by dilute potassium hydroxide to an *isomeride* of the above compound A; *picrate*, m. p. 192—193°. J. C. W.

Action of *o*-Chlorobenzaldehyde on Nitroamines, and a New Scheme for the Preparation of Acridine Derivatives. FRITZ MAYER and BERTHOLD STEIN (*Ber.*, 1917, **50**, 1306—1321). —It has been shown that, instead of forming a normal Schiff's base, 1-aminoanthraquinone and *o*-chlorobenzaldehyde condense together in the presence of a little copper powder and dry sodium carbonate at 220° to yield, among other products, *o*-1-anthraquinonylamino-

benzaldehyde (A., 1916, i, 843). This abnormal course is ascribed to the repression of the basic functions of the amino-group, owing to the proximity of the carbonyl group, and to the weak attachment of the chlorine atom in the aldehyde. Other feebly basic amines should react, under the same conditions, in the same way, and therefore nitro-amines have been examined in this connexion. Generally speaking, a nitro-group in the ortho-position influences the reaction in the abnormal way, otherwise Schiff's bases are produced. The 2-*o*-nitroanilinobenzaldehydes can be condensed to nitroacridines by means of concentrated sulphuric acid.

The above principle can be employed in the synthesis of acridine itself. Iodobenzene and *o*-aminobenzaldehyde are boiled together in nitrobenzene with anhydrous sodium carbonate and some copper powder, the solvent is then removed in a current of steam, the residue is warmed with concentrated sulphuric acid, and finally the solution is diluted and rendered ammoniacal.

The same operations were carried out with *o*-chlorobenzaldehyde and nitro-bases, as follows.

o-Nitroaniline.—The primary condensation product cannot be crystallised, but the crude material yields 1-*nitroacridine*, in silvery leaflets, m. p. 167°, which induces sneezing, and may be oxidised to the known 1-nitroacridone.

m-Nitroaniline.—This base reacts in the usual way to form a Schiff's compound. As prepared by the above method, 2′-*chloro-3-nitrobenzylideneaniline*, $NO_2 \cdot C_6H_4 \cdot N:CH \cdot C_6H_4Cl$, forms grey leaflets, m. p. 116—117°, but if the condensation is carried out under the usual conditions, pale brown needles, with the same m. p., are obtained.

p-Nitroaniline yields 2′-*chloro-4-nitrobenzylideneaniline*, grey leaflets, m. p. 136·5°.

2 : 4-Dinitroaniline.—The primary product is 2-op-*dinitroanilinobenzaldehyde*, $CHO \cdot C_6H_4 \cdot NH \cdot C_6H_3(NO_2)_2$, m. p. 194°, and this is readily converted into 1 : 3-*dinitroacridine*, brown crystals, m. p. 274°.

Under the above conditions, 3-nitro-*p*-toluidine yields a *double compound* of the Schiff's base and the aldehyde, which forms brownish-yellow crystals, m. p. 127°. If potassium carbonate or sodium acetate is used instead of sodium carbonate, the main product is the Schiff's base, and this is formed when the components are merely warmed together. 2′-*Chloro-3-nitrobenzylidene*-p-*toluidine* has m. p. 145°. On the other hand, if less nitrobenzene and *o*-chlorobenzaldehyde are used in the condensation, the aldehydo-base is obtained almost pure. Pure 2-m-*nitro*-p-*toluidinobenzaldehyde* is obtained by condensing *o*-aminobenzaldehyde with 4-chloro-3-nitrotoluene under the above conditions. It crystallises in dark brown leaflets, m. p. 123°, forms an *oxime*, m. p. 160—161°, and may be converted into 1-*nitro-3-methylacridine*, brown needles, m. p. 201—202°, which yields 1-*nitro-3-methylacridone*, glistening, red crystals, m. p. 250°, on oxidation. A mixture of the aldehyde and the Schiff's base in

equimolecular quautities crystallises as the above double compound, m. p. 127°.

4-Nitro-α-naphthylamine yields *2′-chloro-4-nitrobenzylidene-α-naphthylamine*, in pale brown scales by the above condensation, or pale yellow needles by the usual method. m. p. 171°.

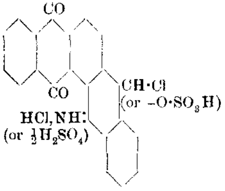
1-Nitro-β-naphthylamine forms *2′-chloro-1-nitrobenzylidene-β-naphthylamine*, in pale brown crystals, m. p. 170—171°.

o-Chlorobenzaldehyde also condenses with 1-amino-2-methylanthraquinone under the above conditions, yielding *o-2-methylanthraquinonylaminobenzaldehyde*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_2Me\cdot NH\cdot C_6H_4\cdot CHO,$$

in reddish-brown crystals.

o-1-Anthraquinonylaminobenzaldehyde also undergoes internal condensation, but not to the acridine. Apparently, water is not lost, the product being an acridol. This is suggested by the fact that esters can be isolated. Thus, if the aldehydo-amine is heated with a solution of hydrogen chloride in glacial acetic acid at 100°. the *hydrochloride* of *anthraquinonyldihydroacridyl* chloride (annexed formula) may be isolated, in brown crystals, which gradually lose hydrogen chloride on exposure to the air, leaving the free *ester*. A *zincochloride* of the same ester may be obtained, in dark brown leaflets, if zinc chloride is mixed with the acetic acid. Similarly, a *sulphate* of the *sulphuric ester* (same formula) may be isolated. When these salts are mixed with ammonia, it appears that the free dihydroacridol immediately suffers oxidation, the product being anthraquinonylacridone, brownish-red crystals. By a mere chance, a blue compound was once isolated which corresponded better with the acridol.



J. C. W.

Quinolyl Pyrryl Ketones and Quinolylpyrrylcarbinols.

P. KARRER (*Ber.*, 1917, **50**, 1499—1508).—A record of syntheses of compounds showing structural resemblance to quinine, an especial point being that the secondary alcohol group is attached to two cyclic systems, as in quinine.

4-Quinolyl 2-pyrryl ketone, $N{<}^{-C_6H_4-}_{CH\cdot CH}{>}C\cdot CO\cdot C{<}^{CH-CH}_{NH\cdot CH}$, pale yellow needles, m. p. 153°, prepared by the action of cinchoninoyl chloride hydrochloride in benzene on ethereal magnesium pyrryl iodide, is reduced in aqueous acetic acid by zinc dust and hydrochloric acid, with formation of *4-quinolyl-2-pyrrylcarbinol*,

$$N{<}^{-C_6H_4-}_{CH\cdot CH}{>}C\cdot CH(OH)\cdot C{<}^{CH-CH}_{NH\cdot CH}$$

colourless crystals, m. p. 177°, which is decomposed by excess of mineral acid, giving a resinous product analogous to pyrrole-red; the parent ketone is soluble without decomposition in dilute hydrochloric acid, giving a yellow solution.

Quinoyl chloride, $\left.\begin{matrix}CH{:}C(COCl)\\CH{=}{=}{=}N\end{matrix}\right>C_6H_4\cdot OMe$, obtained as the *hydrochloride* in the form of a yellow powder by the action of thionyl chloride on quinic acid, reacts with magnesium pyrryl iodide with formation of 4-(6-*methoxyquinolyl*) 2-*pyrryl ketone*,

$$N\left<\begin{matrix}C_6H_3(OMe)\\CH{-}{-}CH\end{matrix}\right>C\cdot CO\cdot C\left<\begin{matrix}CH{-}CH\\NH\cdot CH\end{matrix}\right.,$$

colourless needles, m. p. 153°, which is stable towards excess of mineral acid, giving yellow solutions (*hydrochloride*, colourless; *tribromo*-derivative, $C_{15}H_9O_2N_2Br_3$, yellow needles). The yellow *silver* salt failed to enter into reaction with ethyl iodide, but the expected *N*-ethyl compound is obtainable, although in poor yield, by using magnesium 1-ethylpyrryl iodide in the general synthetic process. Reduction of this ketone is effected in a similar manner to that successful with the quinolyl compound, the resulting 4-(6-*methoxyquinolyl*)-2-*pyrrylcarbinol*,

$$N\left<\begin{matrix}C_6H_3(OMe)\\CH{-}{-}CH\end{matrix}\right>C\cdot CH(OH)\cdot C\left<\begin{matrix}CH{-}CH\\NH\cdot CH\end{matrix}\right.,$$

forming a colourless, crystalline powder, m. p. 174°, which dissolves without decomposition in the calculated quantity of hydrochloric acid, but is rapidly converted into a red resin by excess.

6-*Ethoxyquinoline*-4-*carboxylic acid* is obtained by oxidation of ethyldihydrocupreine, and is further converted into the corresponding *acid chloride hydrochloride*, $\left.\begin{matrix}CH{:}C(COCl)\\CH{=}{=}{=}N\end{matrix}\right>C_6H_3\cdot OEt,HCl$, by the action of thionyl chloride. The latter product reacts with magnesium pyrryl iodide, yielding 4-(6-*ethoxyquinolyl*) 2-*pyrryl ketone*, $N\left<\begin{matrix}C_6H_3(OEt)\\CH{-}{-}CH\end{matrix}\right>C\cdot CO\cdot C\left<\begin{matrix}CH{-}CH\\NH\cdot CH\end{matrix}\right.$, colourless needles, m. p. 139°, which produces yellow solutions in acids, and is reducible by zinc dust and hydrochloric acid in the presence of aqueous acetic acid with formation of 4-(6-*ethoxyquinolyl*)-2-*pyrrylcarbinol*,

$$N\left<\begin{matrix}C_6H_3(OEt)\\CH{-}{-}CH\end{matrix}\right>C\cdot CH(OH)\cdot C\left<\begin{matrix}CH{-}CH\\NH\cdot CH\end{matrix}\right.,$$

a colourless, crystalline mass, m. p. 185°; this, on treatment with excess of mineral acid, is converted into red, resinous products.

4-(6-*Methoxyquinolyl*) 2-(3:5-*dimethylpyrryl*) *ketone*,

$$N\left<\begin{matrix}C_6H_3(OMe)\\CH{-}{-}CH\end{matrix}\right>C\cdot CO\cdot C\left<\begin{matrix}CMe\cdot CH\\NH{-}CMe\end{matrix}\right.,$$

prepared from quinoyl chloride hydrochloride and magnesium 3:5-dimethylpyrryl iodide, is an almost colourless, crystalline mass which gives yellow solutions in mineral acids, and is reducible in

the usual manner to the corresponding 4-(6-*methoxyquinolyl*)-2(3:5-*dimethylpyrryl*)-*carbinol*; this cannot be obtained crystalline, and although it is not reddened by acids, it responds to the pine-shaving test.

The antipyretic action of 4-(6-methoxyquinolyl)-2-pyrrylcarbinol was examined and found to be but slight. It is probable that the corresponding pyrrolidine compound, both chemically and physiologically, would approach more closely to quinine, but the necessary reduction process has not yet been satisfactorily accomplished.

D. F. T.

The Mechanism of the Synthesis of Crystal Violet. P. KARRER (*Ber.*, 1917, **50**, 1497—1499).—It has already been shown that in the coupling of tertiary amines with diazonium salts, attachment of the latter to the former first occurs at the nitrogen atom, after which the azo-radicle migrates to the nucleus. From the observation that Michler's ketone, and also tetraethyldiaminobenzophenone, will undergo condensation with dimethylaniline, diethylaniline, and dipropylaniline, but not with dibutyl- or di*iso*amyl-aniline, and that condensation in the usual way with the aid of phosphoryl chloride fails with *o*-chlorodimethylaniline and dimethyl-*o*-toluidine, but occurs quantitatively with the corresponding meta-isomerides, the conclusion is drawn that the formation of the final product is preceded by an intermediate coupling at the nitrogen atom, the changes being represented:

$$(NMe_2\cdot C_6H_4)_2CCl_2 + NMe_2Ph \longrightarrow (NMe_2\cdot C_6H_4)_2CCl\cdot NClMe_2Ph$$
$$\longrightarrow (NMe_2\cdot C_6H_4)_2CCl\cdot C_6H_4\cdot NMe_2 + HCl \longrightarrow$$
$$(NMe_2\cdot C_6H_4)_2C{:}C_6H_4{:}NMe_2Cl.$$

The effect of the butyl and *iso*amyl radicles attached to the nitrogen atom, and of the chlorine atom or methyl group in the ortho-position, is explained by the steric hindrance offered to the primary attachment of the chloro-compound at the nitrogen atom.

D. F. T.

Cyclic Azoxy-compounds. II. FRITZ ARNDT and BRUNO ROSENAU (*Ber.*, 1917, **50**, 1248—1261. Compare A., 1913, i, 1394).—In the earlier paper, it was shown that *o*-nitrophenylguanidine can be prepared by the condensation of *o*-nitroaniline with cyanamide under the influence of concentrated hydrochloric acid. This reaction can be applied to the production of negatively substituted guanidines in general. The following examples are described: m-*nitrophenylguanidine*, yellow leaflets, m. p. 145° (*nitrate*, m. p. 203°); p-*nitrophenylguanidine*, orange-red leaflets, m. p. 188°; *αα-diphenylguanidine*, $NPh_2\cdot C(NH_2){:}NH$, m. p. 142° (*nitrate*, long, white needles, m. p. 207°); *β-naphthylguanidine*, m. p. 140° (*nitrate*, m. p. 154°); *benzoylphenylguanidine*,

$$NHPh\cdot C(NHBz){:}NH,$$

from aniline and benzoylcyanamide, m. p. 199°; *benzoyl*-m-*nitrophenylguanidine*, pale yellow, velvety needles, m. p. 232°; *benzoyl*-p-*nitrophenylguanidine*, m. p. 219°.

The chief subject of the earlier paper, however, was a reaction which *o*-nitrophenylguanidine and *o*-nitrophenylcarbamide suffer when boiled with dilute alkali hydroxides. Ring closure was shown to occur through the elimination of water, the participating groups being the nitro- and amino-groups. The products are therefore 1 : 2 : 4-benzotriazine-1-oxides. Further examples of this reaction are now given.

One of the new nitro-compounds under investigation is *o*-nitrophenylthiocarbamide, which could not be obtained hitherto. For the preparation of this, *o*-nitroaniline is boiled with thiocarbonyl chloride, when *o-nitrophenylthiocarbimide* is obtained in glistening yellow leaflets, m. p. 73—74°, which reacts with alcoholic ammonia to form the desired product. *o-Nitrophenylthiocarbamide*,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CS \cdot NH_2,$$

forms yellow crystals, m. p. 136°, which give bright red solutions in alkali hydroxide. When mercuric chloride is added to the alkaline solution, *o*-nitrophenylcyanamide is formed, and this method supersedes the earlier mode of preparation (*ibid.*). If the aqueous alkaline solution is boiled, *3-thiol-1 : 2 : 4-benztriazine 1-oxide*, $C_6H_4<\begin{matrix}NO:N\\N{=}C\cdot SH\end{matrix}$, is obtained, in dark red needles, m. p. 184°, which forms a greenish-yellow *methyl ether*, m. p. 123°, and may be oxidised by ammoniacal ferricyanide to the *disulphide*, $C_{14}H_8O_2N_6S_2$, m. p. 205°. (Ring-closure does not follow if the alcoholic alkaline solution is boiled; the product is *o*-nitrophenylcyanamide.) The azoxy-compound may be converted into the pale yellow *3-thiol-1 : 2 : 4-benztriazine*, m. p. 208—209°, by reduction with zinc dust and dilute sodium hydroxide; the corresponding *methyl ether*, $C_6H_4<\begin{matrix}N:N\\N:C\cdot SMe\end{matrix}$, yellow needles, m. p. 104°, is obtained by reducing the methylated azoxy-compound.

The above *o*-nitrophenylthiocarbimide was also warmed with aniline and a small quantity of aniline hydrochloride (as a catalyst), when *o-nitrodiphenylthiocarbamide*, $NO_2 \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, was obtained, in yellow crystals, m. p. 142°. If an alcoholic-ammoniacal solution of this is boiled with mercuric oxide, it yields *o-nitro-αβ-diphenylguanidine*, in yellow needles, m. p. 115°, and this may be converted by boiling with sodium hydroxide into *3-anilino-1 : 2 : 4-benztriazine 1-oxide*, $C_6H_4<\begin{matrix}NO:N\\N{=}C\cdot NHPh\end{matrix}$; this crystallises in orange-red needles, m. p. 197°, and may be reduced to *3-anilino-1 : 2 : 4-benztriazine*, orange-red needles, m. p. 197° (mixture melts 20° lower).

The fact that these cyclic azoxy-compounds can be reduced to azo- and hydrazo-compounds (earlier paper and above examples) illustrates their analogy to ordinary azoxy-compounds. This is confirmed by the reverse process, namely, the oxidation of the benztriazines to azoxy-compounds by means of hydrogen peroxide. If Angeli's formula for azoxy-compounds is correct (A., 1913,

i, 658), these cyclic compounds should give two isomeric azoxy-derivatives, the nitrogen atoms of the –N:N– group being differently linked. The products obtained by the action of 33% hydrogen peroxide and glacial acetic acid on 3-amino- and 3-anilino-1:2:4-benztriazine are actually the isomerides of the oxides formed by ring-closure of the nitrated guanidines, which strongly supports Angeli's views. 3-*Amino*-1:2:4-*benztriazine* 2-*oxide*,

$$C_6H_4{<}\begin{matrix}N{:}NO\\ \quad | \\ N{:}C\cdot NH_2\end{matrix}$$

yellow needles, m. p. 187°, is much less basic than the 1-oxide, and is decomposed by boiling sodium hydroxide, but both isomerides behave alike on reduction. 3-*Anilino*-1:2:4-*benztriazine* 2-*oxide* has m. p. 163°.

The action of nitrous acid on 3-amino-1:2:4-benzotriazine has also been studied. In sulphuric acid solution, the main product is 3-*hydroxy*-1:2:4-*benztriazine*, which crystallises in yellowish-brown needles, m. p. 209—210°, and may be obtained alternatively by reducing 3-hydroxy-1:2:4-benztriazine 1-oxide (*loc. cit.*). The replacement of the amino-group by halogens cannot be effected to any considerable extent through the ordinary diazo-reactions, but with potassium ferro- and ferri-cyanide present, a 10% yield of 3-*chloro*-1:2:4-benztriazine may be obtained, in glistening, yellow leaflets, m. p. 100—101°, which irritates the skin, and a similar yield of the 3-*bromo*-compound, m. p. 122°. J. C. W.

The Conversion of Ethyl Acetoacetate into Hydrazidine Derivatives. CARL BÜLOW and RICHARD HUSS (*Ber.*, 1917, **50**, 1478—1496).—An extension of the earlier knowledge that ethyl acetoacetate by conversion into its benzeneazo-derivative and treatment of this with chlorine can be made to yield an oxalic or glyoxylic acid derivative of the structure NHPh·N:CCl·CO_2Et, the chlorine of which is replaceable by the amino- and analogous radicles with formation of hydrazidine compounds of the general formula NHPh·N:C(NHR)·CO_2Et (Bülow and Neber, A., 1913, i, 207, 910, 999; 1916, i, 845).

Ethyl α-*methylaminoglyoxylate* 2:4-*dichlorophenylhydrazone*, $C_6H_3Cl_2$·NH·N:C(NHMe)·CO_2Et, obtained by the interaction of ethyl α-chloroglyoxylate 2:4-dichlorophenylhydrazone and methylamine in alcoholic solution, forms orange-yellow crystals, m. p. 90°, gives a yellow solution in cold sulphuric acid without decomposition, and yields a colourless *hydrochloride*.

Ethyl α-*ethylaminoglyoxylate* 2:4-*dichlorophenylhydrazone*, $C_6H_3Cl_2$·NH·N:C(NHEt)·CO_2Et, is obtained by a similar reaction, using ethylamine; the product forms yellow needles, m. p. 95°. *Ethyl* α-n-*propylaminoglyoxylate* 2:4-*dichlorophenylhydrazone*, $C_6H_3Cl_2$·NH·N:C(NHPr$^{\alpha}$)·CO_2Et, golden-yellow rhombic crystals, m. p. 102°, prepared in an analogous manner, when treated in

alcoholic solution with chlorine yields a diazo-compound which couples with β-naphthol or *R*-salt, giving red precipitates, and is probably produced by the reaction

$$C_6H_3Cl_2\cdot NH\cdot N\colon C(NHPr^{\alpha})\cdot CO_2Et + 2Cl_2 = HCl + C_6H_3Cl_2\cdot N_2Cl + NHPr^{\alpha}\cdot CCl_2\cdot CO_2Et;$$

a similar reaction is shown by other members of this group of substances.

Other analogous compounds prepared in a similar manner were *ethyl α-n-butylaminoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_4H_9)\cdot CO_2Et$, yellow needles, m. p. 89°; the isomeric *ethyl α-isobutylaminoglyoxylate 2 : 4-dichlorophenylhydrazone*, canary-yellow needles, m. p. 68·5°; *ethyl α-isoamylaminoglyoxylate 2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_5H_{11})\cdot CO_2Et,$$

lemon-yellow needles, m. p. 65·5° (*hydrochloride*, colourless; *platinichloride*, yellow needles); *ethyl α-benzylaminoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot CH_2Ph)\cdot CO_2Et$, yellow needles, m. p. 89°; *ethyl α-anilinoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NHPh)\cdot CO_2Et$, yellow needles, m. p. 90°; *ethyl α-p-anisidinoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_6H_4\cdot OMe)\cdot CO_2Et$, golden-yellow, silky needles, m. p. 158°; *ethyl α-p-phenetidinoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_6H_4\cdot OEt)\cdot CO_2Et$, golden-yellow needles, m. p. 163; *ethyl α-o-toluidinoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_6H_4Me)\cdot CO_2Et$, yellow needles, m. p. 130°; *ethyl α-p-toluidinoglyoxylate 2 : 4-dichlorophenylhydrazone*, m. p. 130°; *ethyl α[α-naphthylamino]-glyoxylate 2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_{10}H_7)\cdot CO_2Et,$$

greenish-yellow platelets, m. p. 130°; *ethyl α[β-naphthylamino]-glyoxylate 2 : 4-dichlorophenylhydrazone*, orange needles, m. p. 161°; in the case of the preparations involving the use of aromatic amines, it was found necessary to heat the amine with the ethyl α-chloroglyoxylate 2 : 4-dichlorophenylhydrazone in the absence of a solvent. *Ethyl α-piperidinoglyoxylate 2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N\colon C(NC_5H_{10})\cdot CO_2Et,$$

colourless needles, m. p. 124°, and *ethyl α-camphylaminoglyoxylate 2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_{10}H_{17})\cdot CO_2Et$, brownish-yellow needles, m. p. 111—111·5°, were also prepared, as also, by the use of α-chloroglyoxylamide 2 : 4-dichlorophenylhydrazone in place of the corresponding ester, was *α-piperidinoglyoxylamide 2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N\colon C(NC_5H_{10})\cdot CO\cdot NH_2,$$

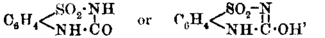
pale yellow needles, m. p. 172°.

Of the "hydrazidine" compounds described above, those derived from aromatic amines are so feebly basic that they dissolve only in strongly acid solutions. All, when dissolved in sulphuric acid, give colorations with oxidising agents such as ferric chloride or

hydrogen peroxide; in dilute solution, sodium nitrite gives a violet-brown coloration or turbidity, the formation of which can be applied as a test for distinguishing between nitrate and nitrite.

D. F. T.

Hydrazides and Azides of Sulphocarboxylic Acids. II. Rearrangement of *o*-Aminosulphonylbenzoyl Azide. ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], **95**, 392—396. Compare A., 1917, i, 709).—*o*-Aminosulphonylbenzoyl azide does not yield the carbimide, $NH_2\cdot SO_2\cdot C_6H_4\cdot N{:}CO$, when boiled with indifferent solvents, or the corresponding urethane when heated with alcohol, as acid azides usually do, but behaves like 3-nitro-2-carboxybenzoyl azide (A., 1913, i, 472), giving a ring compound. The product, *o-aminosulphonylphenylcarbamic anhydride*,



crystallises in slender, glistening needles, m. p. 287—288°, and is converted by prolonged heating with alcohol at 125° into *ethyl* o-*aminosulphonylphenylcarbamate*, needles, m. p. 137°, and by boiling with aniline into *aniline*-o-*sulphonamide*,

$$NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2.$$

The latter forms stout needles, m. p. 153°, yields a *hydrochloride*, m. p. 201°, and a *benzoyl* derivative, $NH_2\cdot SO_2\cdot C_6H_4\cdot NHBz$, needles, m. p. 198°, and gives a bright red azo-dye with *R*-salt. J. C. W.

The Special Reactions in the Transformation of the Azides of Carboxylic Acids. XIV.—XVII. Conclusion. THEODOR CURTIUS (*J. pr. Chem.*, 1917, [ii], **95**, 327—373. Compare A., 1917, i, 635—639).

[With JOHANNES JANSEN.]—XIV. *Hydrazides of Aspartic and* p-*Aminobenzoic Acids.*—*Aspartic monohydrazide* (*α-amino-β-carboxypropionhydrazide*), $CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot NH_2,H_2O$, is prepared by the action of hydrazine hydrate on asparagine or ethyl hydrogen aspartate hydrochloride; it crystallises in long needles, m. p. about 174°, is very soluble in water but insoluble in organic media, and is easily hydrolysed. Its ammonium and silver salts are unstable, and the *dihydrochloride* is excessively hygroscopic. It yields a *benzylidene* compound, decomp. 219—225°, a *salicylidene* compound, m. p. 226° (decomp.), and a m-*nitrobenzylidene* compound, m. p. 191°, and also condenses with ethyl acetoacetate to form a *compound*,

$$CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et,$$

m. p. 168°, which is hydrolysed by water itself.

Aspartic dihydrazide, $N_2H_3\cdot CO\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot N_2H_3$, is obtained from ethyl aspartate. It is a somewhat hygroscopic, easily hydrolysable solid, m. p. 135° (decomp.), which forms a *trihydrochloride*, a *dibenzylidene* compound, which chars without melting, and a *di*-m-*nitrobenzylidene* compound, m. p. 188°. Anisaldehyde does not give a condensation product, but eliminates hydrazine and forms anisaldazine. When treated with nitrous

acid, the dihydrazide effervesces briskly; the residue, after extracting the product with ether and evaporating the solvent, is changed by boiling with alcohol into a syrup, which reacts with phenylhydrazine to give glyoxalphenylosazone, the product of the decomposition of the acid azide being, therefore, aminoacetaldehyde.

Ethyl *p*-aminobenzoate, m. p. 92°, b. p. about 310°, reacts with hydrazine hydrate to form p-*aminobenzhydrazide*, which crystallises in long needles, m. p. 220°, and yields a *dihydrochloride*, a *benzylidene* compound, silky needles, m. p. 210°, and a *salicylidene* compound, glistening leaflets, m. p. 220°. A hydrochloric acid solution of the hydrazide reacts with *p*-toluenediazonium sulphate to give p-*aminobenzoyl azide*, $NH_2\cdot C_6H_4\cdot CO\cdot N_3$, which separates as a flocculent, crystalline mass. When this is boiled with water or alcohol, it loses one molecular proportion of nitrogen, and the carbimide formed immediately undergoes internal rearrangement into *p*-phenylenecarbamide, $C_6H_4<{NH \atop NH}>CO$.

[With RICHARD COLOSSER.]—XV. *Hydrazides of α- and β-Dimethylaminopropionic, Dimethylaminosuccinic, and Dimethylanthranilic Acids.—Ethyl α-dimethylaminopropionate*, a liquid with the odour of turpentine, b. p. 156·5°, is obtained from the bromo-ester and dimethylamine. It reacts with hydrazine hydrate, forming *α-dimethylaminopropionhydrazide*, a soluble syrup, which yields a *dihydrochloride*, m. p. 214°, and a m-*nitrobenzylidene* compound, radiate needles, m. p. 144°, and reacts with nitrous acid to form acetaldehyde, ammonia or dimethylamine, but not hydrazine, as the volatile products.

Methyl β-dimethylaminopropionate, from the iodo-ester, yields *β-dimethylaminopropionhydrazide* as a yellow syrup, which forms a *dihydrochloride*, m. p. 146—147° (decomp.), and a *benzylidene* compound, m. p. 131·5°, and does not react with nitrous acid to form the acid azide. On keeping, the hydrazide gradually changes into *bis-β-dimethylaminopropionhydrazide*,

$$N_2H_2(CO\cdot CH_2\cdot CH_2\cdot NMe_2)_2,$$

m. p. 115·5°, which forms a *dihydrochloride*, m. p. 126°.

Methyl dimethylaminosuccinate, m. p. 32°, b. p. 115°/18 mm., from the bromo-ester, yields *dimethylaminosuccindihydrazide*, $N_2H_3\cdot CO\cdot CH_2\cdot CH(NMe_2)\cdot CO\cdot N_2H_3$, needles, m. p. 147°, which gives a hygroscopic *trihydrochloride*, m. p. 128°, a *dibenzylidene* compound, m. p. 132°, a *disalicylidene* compound, m. p. 216·5°, and a *diisopropylidene* compound, m. p. 137°, and may be converted into glyoxalphenylosazone, like the above aspartic dihydrazide.

Methyl dimethylanthranilate, m. p. 18·5°, yields *dimethylanthranilhydrazide*, $NMe_2\cdot C_6H_4\cdot CO\cdot N_2H_3$, m. p. 51°, which forms a *dihydrochloride*, m. p. 165—166°, a *benzylidene* compound, m. p. 115°, a yellow *salicylidene* compound, m. p. 103°, and an *isopropylidene* compound, m. p. 150°. The *azide*, $NMe_2\cdot C_6H_4\cdot CO\cdot N_3$, is a very unstable, yellow oil.

[With WALTER DONSELT.]—XVI. *Hydrazides of Tyrosine and*

Benzoyltyrosine.—Tyrosine was obtained by hydrolysing casein, and from *p*-hydroxybenzaldehyde and hippuric acid. The hydrochloride of the ethyl ester may be converted into impure *ethyl α-diazo-β-p-hydroxyphenylpropionate*, $OH \cdot C_6H_4 \cdot CH_2 \cdot CN_2 \cdot CO_2Et$, by the method in use for the preparation of ethyl diazoacetate from glycine. *Tyrosine amyl* ester crystallises in pale yellow needles, m. p. 68—70°, and its *hydrochloride* has m. p. 181—182°. Although tyrosine ethyl ester has the same m. p. whether obtained from casein or synthetically, the two specimens give different *hydrazides*, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot N_2H_3$; the "synthetic" hydrazide forms white needles, m. p. 171°, and yields a *dihydrochloride*, decomp. 235·5°, a *dibenzylidene* compound, m. p. 197°, a *disalicylidene* compound, m. p. 205—206°, and a *diisopropylidene* compound, m. p. 149—150°; the "natural" hydrazide has m. p. 195·5°, but yields the same benzylidene compound. With nitrous acid, it gives a crude azide, m. p. 120—140°, but is largely hydrolysed to tyrosine.

Benzoyltyrosine ethyl ester, bundles of needles, m. p. 122—123°, and *amyl* ester, m. p. 106—107° are described. *Benzoyltyrosine hydrazide*, felted needles, m. p. 229—230°, yields a *benzylidene* compound, very slender needles, m. p. 250—251°, a *salicylidene* compound, m. p. 243—244°, and an iso*propylidene* compound, white needles, m. p. 215—216°, and may be converted into the *azide*, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH(NHBz) \cdot CO \cdot N_3$, m. p. 72—73° (decomp.). This reacts with ammonia to form *α-benzoylamino-β-p-hydroxyphenylpropionamide*, m. p. 232—233°, identical with a product obtained from the ethyl ester; with aniline, to give the *anilide*, m. p. 212°; and with alcohol, to form the urethane, *ethyl α-benzoylamino-β-p-hydroxyphenylpropylcarbamate*, m. p. 171—172°.

[With Nikolaos C. Kyriacou.]—XVII. *Hydrazide and Azide of Dibenzoyl- and Dihippuryl-cystine.*—A convenient preparation of cystine from human hair is described. Cystine methyl ester dihydrochloride yields an impure *α-bisdiazo*-methyl ester,

$$S_2(CH_2 \cdot CN_2 \cdot CO_2Me)_2,$$

and may be de-aminated to *β*-dithiodilactic acid,

$$S_2[CH_2 \cdot CH(OH) \cdot CO_2H]_2,$$

the *calcium* salt of which is a sandy powder.

Dibenzoylcystine methyl ester, m. p. 192—193°, and *ethyl* ester, m. p. 185—186°, form snow-white needles. The *dihydrazide*, $S_2[CH_2 \cdot CH(NHBz) \cdot CO \cdot N_2H_3]_2$, is a crystalline mass, m. p. 206—207°, which forms a *dibenzylidene* compound, m. p. 228—230°, and the impure *diazide* is a white mass, which forms a carbamide, m. p. 178° (decomp.), when boiled with water.

Hippuryl azide and cystine react in *N*-sodium hydroxide solution to form *dihippurylcystine*, $S_2[CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH_2 \cdot NHBz]_2$, which sinters at 65°, intumesces at 120°, and chars at above 160°. The *methyl* ester crystallises in glistening needles, m. p. 113°; the *dihydrazide* decomposes at 160—162°, and forms a *dibenzylidene* compound, m. p. 180° (decomp.), and a *diisopropylidene* compound, m. p. 152—153°; the *diazide* is a very pale pink mass

m. p. 95—97° (decomp.), which yields the *urethane*,

$S_2[CH_2\cdot CH(NH\cdot CO_2Et)\cdot NH\cdot CO\cdot CH_2\cdot NHBz]_2$,

m. p. 168—169°, when boiled with alcohol.

The azides of dibenzoyl- and dihippuryl-cystine change into carbamides when boiled with water. If these are boiled with dilute sulphuric acid, dithiodiacetaldehyde, $S_2(CH_2\cdot CHO)_2$, distils over with the steam, and the remaining liquid becomes dark blue. The same aldehyde is obtained by hydrolysing *dithiobisdiethylacetal*, $S_2[CH_2\cdot CH(OEt)_2]_2$, b. p. 140—170°/14 mm., which is prepared as an evil-smelling oil by heating bromoacetal with potassium hydrogen sulphide and oxidising the product with iodine. The aldehyde forms a characteristic *di*-p-*nitrophenylhydrazone*, a yellowish-red powder, m. p. 176—177°. J. C. W.

Chemical Studies in Physiology and Pathology. I. The Chemistry of the Proteins regarded as the Basis of Vital Processes. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, **83**, 42—61).—A paper of purely theoretical character. The protein is regarded as consisting of an inner core surrounded by layers of adsorbed degradation products of proteins, such as amino-acids and albumoses. It is only when thus surrounded that it exists in a colloidally dispersed condition. Either synthesis or hydrolysis can take place in the adsorbed layer. If hydrolysis takes place, the simpler amino-acids will be formed, and these may pass away; or amino-acids, etc., may be carried to the adsorbed layer, and synthesis take place. The protein molecule thus conceived is supposed to be surrounded by a semipermeable membrane of variable permeability, which regulates the passage of substances to and from the layer of adsorption products. This membrane itself is supposed to be formed from a protein, which, after loosing its adsorbed products, is no longer colloidally dispersed, but becomes insoluble ("denaturated"). The application of this theory to the phenomena of growth, senility, secretion, and immunity is discussed. S. B. S.

Nuclein Metabolism. IV. The Structure of Yeast-nucleic Acid and its Cleavage by Weak Ammoniacal and Fermentative Hydrolysis. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1917, **100**, 121—147. Compare A., 1914, i, 1015).—The triphosphonucleic acid previously obtained by the action of intestinal juice on yeast-nucleic acid has now been prepared by hydrolysis with weak ammonia. After the removal of the ammonia, the hydrolysed yeast-nucleic acid is treated with brucine; three crystalline brucine salts are obtained, which are separated by fractional crystallisation. The least soluble salt is identified as the *brucine* salt of uridine-phosphoric acid, $C_9H_{13}O_9N_2P(C_{23}H_{26}O_4N_2)_2$, m. p. 177°, $[\alpha]_D + 14\cdot 4°$; the most soluble brucine salt is that of the triphosphonucleic acid already described, whilst an optically inactive *brucine* salt is also obtained which apparently is that of dl-*triphosphonucleic acid*,

$C_{29}H_{42}O_{23}N_{13}P_3(C_{23}H_{26}O_4N_2)_6$,

m. p. 185—187°. A repetition of previous work now shows that these three cleavage products are also formed by the action of intestinal juice on yeast-nucleic acid, and are readily separable by the agency of brucine.

The hydrolysis of either of the triphosphonucleic acids by ammonia under pressure yields guanosine, adenosine, and cytidine, whilst the similar hydrolysis of uridine-phosphoric acid liberates the uridine. When yeast-nucleic acid is heated with 2% sulphuric acid at 125°, the triphosphonucleic acids, if formed, are further decomposed, and only the uridine-phosphoric acid appears to be obtainable from the hydrolytic products.

The authors consider that the simultaneous liberation of the trinucleotide, triphosphonucleic acid, and the mononucleotide, uridine-phosphoric acid, indicates that the three constituent mononucleotides in triphosphonucleic acid must be combined in a different manner from the uridine-phosphoric acid in the parent molecule of yeast-nucleic acid. The existence of a hexabrucine salt of triphosphonucleic acid shows that the component mononucleotides must be joined together through the carbohydrate instead of the phosphoric acid radicles (compare Jones and Read, A., 1917, i, 232, 233). *They suggest, therefore, that the constituent mononucleotides* of yeast-nucleic acid are all joined together through the phosphoric acid groups, whilst the mononucleotides composing the triphosphonucleic acid have additional linkings between the carbohydrate groups. Hydrolysis with dilute ammonia severs only the linking between the phosphoric acid groups, and thus the triphosphonucleic acid and uridine-phosphoric acid are obtained.

The authors are unable to ascertain the relative number of triphosphonucleic and uridine-phosphoric acids present in the parent molecule, but since two of the former have been isolated, they depict the structure of yeast-nucleic acid on the supposition that it contains two triphosphonucleic acid and one uridine-phosphoric acid groups in the molecule. H. W. B.

The Influence of Formaldehyde on the Digestion of Proteins. FRITZ JOHANESSOHN (*Biochem. Zeitsch.*, 1917, **83**, 28—41).—Finkelberg's pepsin is not injured after remaining for one day in 10% formaldehyde. The various preparations of trypsin, on the other hand, were weakened in their action after remaining with formaldehyde, trypsinogen, after treatment with 0·05%, and Merks's trypsin after treatment with 1% of the aldehyde. Egg-white after remaining for nine days in 1% aldehyde solution is rendered indigestible by pepsin-hydrochloric acid, and its digestibility by trypsin is diminished by about one-fifth. The relationship of the results obtained by the author to those of other investigators is discussed. S. B. S.

The Theory of Schardinger's Enzyme, and on Reciprocal Influencing of Reducing Agents in some Photochemical Experiments. G. WOKER and H. MAGGI (*Ber.*, 1917, **50**, 1321—1331).—Formaldehyde does not reduce methylene-blue itself

and is able to hinder the reduction of this dye by a number of reductases and also sugars (compare Maggi and Woker, this vol., ii, 22). Schardinger's milk enzyme is peculiar, however, in that formaldehyde does not influence its action on methylene-blue. In the presence of methylene-blue the milk enzyme can also play the part of an oxydase or mutase (compare Wieland, A., 1913, i, 1304). For example, salicylaldehyde is converted into salicyl alcohol and salicylic acid.

These various functions of Schardinger's enzyme are discussed in the light of the author's theory of the aldehydic character of enzymes. As a *reductase*, a "ferment-aldehyde" would react according to the scheme $R_F \cdot CHO + H_2O = R_F \cdot CH(OH)_2 \longrightarrow R_F \cdot CO_2H + 2H$, and, for example, 2H + methylene-blue = leuco-base + H_2O. [R = "ferment-radicle."] As an *oxydase* it would act as an acceptor of hydrogen from easily reducible substances, thus: $R_F \cdot CHO + 2H = R_F \cdot CH_2 \cdot OH$; in the presence of oxygen or substances like methylene-blue or quinone which readily give up oxygen, the ferment-aldehyde would be regenerated and then act further on the reducible substance. As a *mutase* it would react, for example, with salicylaldehyde, thus:

(1) $R_F \cdot CH(OH)_2 + CHO \cdot C_6H_4 \cdot OH = R_F \cdot CO_2H + OH \cdot CH_2 \cdot C_6H_4 \cdot OH$.
(2) $R_F \cdot CO_2H + (OH)_2CH \cdot C_6H_4 \cdot OH = R_F \cdot CH(OH)_2 + CO_2H \cdot C_6H_4 \cdot OH$.

In the presence of substances which readily give up oxygen, more of the ferment-acid, $R_F \cdot CO_2H$, would be formed and, therefore, more salicylic acid.

One aldehyde can act as an acceptor of hydrogen from the hydrate of another aldehyde, and this is what is supposed to happen in the case of formaldehyde and Schardinger's enzyme. The following changes are possible: (*a*) $R_F \cdot CH(OH)_2 + H \cdot CHO = CH_3 \cdot OH + R_F \cdot CO_2H$; (*b*) $R_F \cdot CO_2H + H \cdot CH(OH)_2 = H \cdot CO_2H + R_F \cdot CH(OH)_2$. The reduction of methylene-blue by the mixture of formaldehyde and milk may then be due to the direct action of methyl alcohol, thus: dye + MeOH = leuco-base + $H \cdot CO_2H$; or indirectly thus: $R_F \cdot CHO + MeOH = R_F \cdot CH_2 \cdot OH + H \cdot CHO$, and $R_F \cdot CH_2 \cdot OH$ + dye = $R_F \cdot CHO$ + leuco-compound. It is possible to test whether the direct reduction can proceed, and it may be shown that methyl alcohol does bleach methylene-blue solutions if exposed to the light. Milk bleaches methylene-blue in the dark, however, but not so well as in the light, so other factors are at work in the action of formaldehyde-milk on the dye.

The reduction of methylene-blue also proceeds quickly in the light, in the presence of nitrites, arsenious oxide, or dextrose, but if these agents are mixed with methyl alcohol, little or no bleaching takes place. This remarkable counteraction between pairs of reducing agents is discussed along somewhat similar lines. J. C. W.

Physiological Chemistry.

The Sugar of the Blood. S. GUTMANN and O. ADLER (*Biochem. Zeitsch.*, 1917, **83**, 11—17).—The proteins of the blood were precipitated by Schenk's method, and the reducing action (on copper solutions) of the protein-free blood was determined in the filtrate directly, and after heating with 2·2% hydrochloric acid. No difference was found in the two sets of estimations, whence the conclusion is drawn that the blood contains no polysaccharides. Neither were polysaccharides to be detected when ordinary starch was added to blood, which was then rendered protein-free by Schenk's method. In the case where soluble starch was added, however, the reduction was greater after hydrolysis. S. B. S.

Residual Reducing Power of the Blood. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1917, **100**, 215—220).—Polemical against Griesbach and Strassner (see A., 1917, i, 491). H. W. B.

A New Ferment of the Leucocytes of Blood and Pus: Lipoidase. NOËL FIESSINGER and RENÉ CLOGNE (*Compt. rend.*, 1917, **165**, 730—732).—The leucocytes of blood and of acute suppuration have the property of secreting an enzyme capable of hydrolysing lecithin in feebly alkaline solution. The enzyme is destroyed by heating at 56—60° in half an hour, and does not act in strongly acid or alkaline solution. The red corpuscles in large quantity and apparently normal serum exert an inhibitory action on the enzyme. This lipoidase is distinguished by its thermolability from the lipase occurring in the leucocytes. W. G.

The Presence of Phosphates in Human Blood Serum. II. Acid Soluble (Total) Phosphorus, pre-existing Orthophosphoric Acid, and "Residual" Phosphorus in Normal Cases. JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **83**, 81—95. Compare A., 1917, i, 520).—The difference between the acid-soluble phosphorus and the orthophosphoric acid which can be estimated directly in the serum is called the residual phosphorus. In the sera of healthy individuals it amounts generally to more than 0·5 mg. per 100 c.c. of serum, or 15% of the total acid-soluble phosphorus. The amount is subject to variations. S. B. S.

Estimation of Small Amounts of Calcium, particularly in Blood. JOHN O. HALVERSON and OLAF BERGEIM (*J. Biol. Chem.*, 1917, **32**, 159—170. Compare A., 1916, ii, 270).—Full details are given of the method previously described.

Normal serum contains about 10 mg. of calcium in 100 c.c. of serum. The amount of calcium in human milk varies between 27 and 33 mg. per 100 c.c. H. W. B.

Calcium Content of the Blood-serum in certain Pathological Conditions. JOHN O. HALVERSON, HENRY K. MOHLER, and OLAF BERGEIM (*J. Biol. Chem.*, 1917, **32**, 171—179. Compare preceding abstract).—In nearly all pathological conditions the amount of calcium in the blood-serum does not differ appreciably from that found in health. Slight decreases are observed in some cases of uræmia, eclampsia, and pneumonia. H. W. B.

Diffusion of Electrolytes through the Membranes of Living Cells. V. Additive Effect of Salt and Base and the Antagonistic Effect of Salt and Acid. JACQUES LOEB (*J. Biol. Chem.*, 1917, **32**, 147—158. Compare A., 1917, i, 102).—The author has previously shown that the effects of the addition of a second salt on the diffusion of potassium salts through the membranes of *Fundulus* eggs are analogous to the effects of salts on globulins, which are insoluble in water, soluble in a moderate concentration, and insoluble again in a very high concentration of salt. It is suggested that the diffusion of potassium salts is dependent, *therefore, on the solution of a certain constituent of the membrane* with properties resembling those of a globulin. This hypothesis is supported by the analogy which is now shown to exist between the effects of salt on the action of acids and bases in the case of the *membrane of the Fundulus egg and in that of globulins* respectively.

When *Fundulus* eggs are put into solutions of bases not sufficiently concentrated to injure the embryo, the bases become injurious when neutral salts in low concentrations are added. An additive effect of salt and base is observed also at higher concentrations of the base. On the other hand, the addition of a neutral salt to an acid which kills rapidly the embryo of *Fundulus* eggs produces an antagonistic effect, which is also observed for lower concentrations of acids. The minimal quantity of a salt required for these effects diminishes with an increase in the valency of both anion and cation of the salt. By comparing the effects on the egg with those on the newly-hatched embryo, it is shown that these additive and antagonistic effects are due, in the case of the egg of *Fundulus*, to an influence of the salt on the rate of diffusion of alkali and acid through the membrane of the egg, accelerating the diffusion of alkali and retarding the diffusion of acid. Since, therefore, salts increase the rate of diffusion of certain electrolytes through the membrane of the egg of *Fundulus* when they are also able to dissolve globulins, and they retard or inhibit the diffusion when they are likely to prevent the solution of globulins, it is probable that the substance in the membrane on which the diffusion of electrolytes depends is a globulin. H. W. B.

Cholesterol in Animal Organs. I. LIFSCHÜTZ (*Biochem. Zeitsch.*, 1917, **83**, 18—27).—Cholesterol was prepared from oxbrain in the usual manner, and sufficient digitonin was added to the alcoholic solution to precipitate about one-third to one-half of

the cholesterol. From this precipitate, the ordinary cholesterol could be isolated by Windaus's method. The filtrate from the digitonin-cholesterol compound yielded, however, a cholesterol which crystallised in an elliptical form and melted after repeated recrystallisations from ethyl and methyl alcohols at 139—141°, or 5° below the m. p. of the ordinary form. From ox-blood, cholesterol was also prepared, and this consisted chiefly of the substance with elliptical form (m. p. 139—141°), from which the acetate (m. p. 109—110°) was prepared. The latter melts about 4° below the acetate of the ordinary cholesterol. The cholesterol of the organs mostly concerned in the resorption of fat consists for the greatest part of ordinary (rhombic) cholesterol, whereas the cholesterol of the kidneys is almost exclusively of the elliptical form. S. B. S.

Metabolism of Sugar in the Central Nervous System. ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1917, **100**, 185—202).—When the spinal cords of frogs are placed in a saline solution containing dextrose. and oxygen is bubbled through the solution, the dextrose gradually disappears. In the absence of the spinal cords, the dextrose content of the solution remains unchanged. The nerve tissue is therefore capable of inducing glycolysis. The membranes surrounding the spinal cord appear to be impermeable to dextrose, because the glycolysis becomes more pronounced when the membranes are removed before placing in the dextrose-saline solution. In these circumstances, at the ordinary temperature, from 4 to 5 mg. of dextrose per 1 gram of cord disappear in twenty-four hours. The glycolysis varies with the temperature and gradually declines throughout the experiment, being no longer recognisable after the second day. The latter observation indicates that the results cannot be attributed to bacterial action. Lack of oxygen rapidly causes an irreversible decline in the glycolysis; alcohol, ethyl carbamate, and also a trace of a soluble calcium salt (0·1% calcium chloride) lower the glycolysis, but after the removal of the inhibiting agent, it rapidly returns to its former level. Electrical stimulation of the tissue evokes a great acceleration of the rate of disappearance of the dextrose, which reaches twice the normal value.

If the spinal cords are reduced to a fine state of division, the rate of glycolysis is markedly increased, presumably on account of the increased surface of contact between tissue and dextrose solution. It is a function of the living tissue; the boiled material does not induce any glycolysis. The consumption of dextrose by the minced spinal cord is influenced in the same way as in the case of the intact organ by the various factors above described, with the exception that electrical stimulation does not evoke any increase in glycolysis after the normal structure of the tissue has been destroyed. H. W. B.

The Carbohydrate Metabolism in the Surviving Liver of the Dog. J. ABELIN and J. M$^{A.}$ DE CORRAL (*Biochem. Zeitsch.*, 1917, **83**, 62—73).—Although the perfusion of peptone solution has no influence on the glycogen content of the liver of a rabbit, it diminishes the amount of this carbohydrate in the liver of the dog. Perfusion of adrenaline is withont action on the glycogen degradation in the livers both of the rabbit and the dog.

S. B. S.

Biological Analysis of Diets Producing Pellagra. II. Minimum Requirements of the two Unidentified Dietary Factors for Maintenance as contrasted with Growth. E. V. MCCOLLUM and N. SIMMONDS (*J. Biol. Chem.*, 1917, **32**, 181—194).—The authors describe feeding experiments on rats in which the relative and absolute quantities of the two factors, "fat-soluble A" and "water-solnble B," in the diet are varied. The former factor is contributed in the form of butter-fat and the latter in wheat-germ, and it is found that 1% of each of these factors in the diet is just sufficient to maintain the weight of adult rats. In these circumstances, however, the life of the animal is uncertain, and the rats may die unexpectedly without any apparently sufficient cause. The life of young rats may be maintained for considerable periods without growth when minimum amounts of the two factors are present, and, subsequently, growth may occur in proportion to the increased amounts of the factors administered. The extent of growth depends on the amount of that factor which is present in relatively the smaller proportion; in other words, increased growth after an increased proportion of "fat-soluble A" does not occur unless the amount of "water-soluble B" is increased to a corresponding extent. The results are illustrated by numerous charts. H. W. B.

The Significance of the so-called "Steric Hindrance" in Biological Processes. I. The Influence of the Methyl Group in the Ring. OSKAR BAUDISCH and FRANZ KLAUS (*Biochem. Zeitsch.*, 1917, **83**, 6—10).—Attention is directed to the fact that substances containing a methyl group are less reactive biologically than the corresponding substances without this group. The statement is illustrated by reference to the therapeutic action of the rosaniline-dyes, of acridine-yellow and trypoflavin, and of atoxyl and its methyl derivatives. In all cases, the more methyl groups a substance contains, the smaller its therapeutic activity. Other instances quoted are the differences between crystal-violet and new-magenta when used as stains by Gram's method, and the differences between chrysarobin and cignolin (non-methylated substance) when employed, according to Unna, for the treatment of psoriasis.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. IV. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **83**, 74—80. Compare A., 1917, i, 528).—In the last communication, it was shown that urease is produced by bacteria which are grown on a medium containing inorganic salts and glycerol, ammonium lactate, sodium aspartate, and leucine, of which the last-named is indispensable. Further investigations have been undertaken to ascertain whether all the above-mentioned organic substances are indispensable for production of the ferment. On leucine alone, a certain amount of ferment is produced, but more satisfactory amounts are obtained when the medium contained, in addition to leucine, glycerol and sodium aspartate, or ammonium lactate and sodium aspartate. When sodium lactate alone is employed, even after transference of the bacteria to a medium containing leucine, scarcely any urease is produced. It is to be recalled that bacteria will grow on a medium containing no leucine, but produce no urease. On transference to a medium containing leucine, however, the ferment is formed. In the experiments described in this paper, the bacteria were first grown on media containing various mixtures of the above-named organic substances (sometimes with the addition of leucine), and then, after the second generation of growth, transferred to a medium containing this amino-acid. In the control experiments where this acid was not present, no urease was produced. S. B. S.

The Extraction of Invertase and Maltase from the Permanent Yeast Preparations made by the Acetone Method. EDUARD BUCHNER and FERDINAND REISCHLE (*Biochem. Zeitsch.*, 1917, **83**, 1—5).—The preparations were washed, and then allowed to act on sugars. No evolution of carbon dioxide took place unless boiled juice were added (to replace the co-enzyme which had been washed out). More carbon dioxide was evolved when dextrose and maltose were added than in the case when the same washed preparation was treated with sucrose, and these experiments indicate that the invertase and maltase can be removed by washing. S. B. S.

Formation of Hexosephosphate during Alcoholic Fermentation. HANS EULER, OLOF SVANBERG, GRETA HALLBERG, and KARIN BRANDTING (*Zeitsch. physiol. Chem.*, 1917, **100**, 203—208). —On estimating, at intervals of fifteen minutes, the amount of inorganic phosphate present in a fermenting mixture of dextrose, yeast, and disodium hydrogen phosphate, it is found that during the first half of the fermentation the phosphate remains almost unchanged whilst subsequently rapid combination with dextrose

occurs. The acidity of the mixture remains practically constant throughout the whole period of fermentation. It is suggested that during the first half of the time of reaction a catalyst is formed which accelerates the combination of dextrose and phosphate during the later stages of fermentation. H. W. B.

Action of Sodium Phosphate on the Lactic Acid Fermentation. HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1917, **100**, 148—158).—The lactic acid fermentation of dextrose by the agency of *Bacterium casei*, E., is accelerated by sodium dihydrogen phosphate and inhibited by trisodium phosphate, but a conversion of the inorganic phosphate into hexosephosphate, such as occurs during the fermentation of dextrose by yeast, cannot be detected. The intermediate formation of lactic acid during the alcoholic fermentation of dextrose occurs, therefore, if it occurs at all, by a process which is probably different from that which is effected by the lactic acid bacilli. H. W. B.

Amygdalin as Nutriment for Fusarium. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 185—188).—Amygdalin is assimilated by *Fusarium*, young mycelium being formed, but the addition of emulsin to the amygdalin solution entirely prevents growth. Amygdalin is as satisfactory a nutrient as dextrose in respect to the dry weight of mould obtained.

W. G.

The Chemistry of the Higher Fungi. XII. Lenzites sepiaria, Sw., Panus stypticus, BULL., and Exidia auricula Judæ, FR. JULIUS ZELLNER (*Monatsh.*, 1917, **38**, 319—330. Compare A., 1915, i, 1086).—Extraction of *Lenzites sepiaria*, Sw., collected from pine trunks, with light petroleum, yielded a yellowish-brown, fatty oil containing an ergosterol; on extraction with ether, an ergosterol was obtained, together with a yellowish-red resin soluble in aqueous alkali hydroxide. The alcoholic extract was separated into constituents soluble in water, these including mannitol and mycose [trehalose] with small quantities of choline and dextrose, and a fraction insoluble in water containing brown nitrogen-free amorphous substances. The aqueous extract of the fungus contained a carbohydrate which did not reduce Fehling's solution, together with a trace of quinoline and mineral substances. Hydrolysis of the leathery residue insoluble in the above solvents gave rise to dextrose as the main product, together with mannose and glucosamine; indications of pentosans were also observed.

Panus stypticus, Bull., gave similar results, except that two carbohydrates were observed in the aqueous extract, which agreed in properties with Boudier's viscosin and mycetide (these substances have never yet been obtained in a state of purity), and that glucosamine was the only definite substance isolated from the residual insoluble tissue.

With *Exidia auricula Judae*, Fr., similar observations were

made, but no mannose or mycetide was detected in the alcoholic and aqueous extracts respectively; the viscous constituent in the aqueous extract on hydrolysis yielded mannose with a little dextrose, and on oxidation with nitric acid produced only oxalic acid; it is therefore probable that the mucous substance is a mannan. D. F. T.

The Relationship which Exists, in Plant Tissues, between the Acid and Basic Elements. G. André (*Bull. Soc. chim.* 1917, [iv], **21**, 258—271).—A more detailed account of work already published (compare A., 1912, ii, 675, 803; 1913, i, 233, 688, 946). W. G.

The Transient Red Colour given by certain Leaves when Treated with Nitric Acid in the Xanthoproteic Test. Otto Gertz (*Biochem. Zeitsch.*, 1917, **83**, 129—132).—The author is in agreement with Lakon (A., 1917, i, 504) that the colour in question can be due to anthocyanin. In certain plants, however the colour is specific for nitric acid, and is not given by other acids, and in these cases it cannot be due to anthocyanin. The author ascribes it to a nitroso-derivative of some substance as yet unidentified. The nitroso-derivative is formed by reduction, and on further reduction it becomes colourless. S. B. S.

A New Plant containing Hydrogen Cyanide, Isopyrum fumarioides, L. Marcel Mirande (*Compt. rend.*, 1917, **165**, 717—718).—*Isopyrum fumarioides* contains a cyanogenetic glucoside and an enzyme capable of hydrolysing it. The plant when in full flower and nearly in fruit yields 0·249 gram of hydrogen cyauide from 100 grams of fresh plant material. The green fruits contain 0·115% of hydrogen cyanide. The younger the plant, the greater is the content of hydrogen cyanide. W. G.

Vegetable and Animal Fats and Waxes. I. Fat from Rice Bran. Albert B. Weinhagen (*Zeitsch. physiol. Chem.*, 1917, **100**, 159—166).—Rice bran contains 10·94% of fatty substances soluble in ether. They can be separated into a liquid oil (73%) and a solid fat (27%). The oil contains 5·3% of phytosterol and 91% of fatty acids, of which 59% is oleic and 31·8% palmitic acid. The solid portion consists of 4·7% of phytosterol and 90·6% of fatty acid, which is practically pure palmitic acid. A substance is also present which can be separated from the phytosterol by fractional crystallisation from alcohol, in which it is only slightly soluble. It is found to he a saturated *hydrocarbon*, $C_{27}H_{48}$, m. p. 79·5°—80·5.

Rice bran does not contain any glycerol or any phosphorus compounds soluble in ether, and only a trace of alcohol-soluble phospholipoids. H. W. B.

Organic Chemistry.

Hydrolysis of Organic Haloids and the Corrosion of Metals. HOWARD WATERS DOUGHTY (*J. Amer. Chem. Soc.*, 1917, **39**, 2685—2692).—A qualitative study of the subject. The hydrolysis of carbon tetrachloride by water at ordinary temperatures is negligible, but it is greatly accelerated by the presence of *iron or copper, the acceleration being accompanied by corrosion* of the metal, which is very well marked with iron, but very slight with copper. This corrosion is very greatly increased by the presence of ammonia, but does not take place in the absence of water or carbon tetrachloride. The products are ferric hydroxide and cupric ammonium chloride.

Certain other organic haloids behave in a manner similar to carbon tetrachloride towards copper, the action being most pronounced with compounds containing a trichloromethyl group. Monohalogen derivatives have practically no action on copper in the presence of water and ammonia, and the presence of two halogen atoms gives no increased effect unless they are attached to the same carbon atom. No effect is observed in the case of halogen substituted in the benzene nucleus.

Tetrachloroethylene may be readily detected in that when allowed to remain in contact with water, ammonia, and copper, the aqueous layer develops a rich red colour. W. G.

The Relative Stability of Halogen-substituted Aliphatic Acids in Aqueous Solution. W. A. DRUSHEL and G. S. SIMPSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2453—2460).—The authors are engaged on a study of the kinetics of the action of water on halogeno-aliphatic acids, and have so far investigated the sodium salts of the halogeno-acetic acids. Decinormal solutions of the salts were heated in sealed tubes at constant temperatures of 70—90°, and, after different intervals, the free acid and also the sodium haloid were titrated, or, in the case of the trichloroacetate, the sodium hydrogen carbonate formed according to the equation $CCl_3{\cdot}CO_2Na + H_2O = CHCl_3 + NaHCO_3$.

With the exception of the case of the trihalogeno-acids, the action of water is a true hydroxylation. It is probable that two reactions take place consecutively in the case of the dihalogeno-compounds, thus, $CHCl_2{\cdot}CO_2Na + H_2O = CHO{\cdot}CO_2H + NaCl + HCl$ and $CHCl_2{\cdot}CO_2Na + HCl = CHCl_2{\cdot}CO_2H + NaCl$. As the latter reaction is practically instantaneous, the hydroxylation of the dichloroacetate should appear as a unimolecular reaction, but the observed values do not agree with either a uni- or bi-molecular type. There is found to be more sodium chloride produced than free acid. The

anomaly will be discussed in a later paper (compare also Johanssen, Senter, and others).

The relative stability of these sodium salts in $0 \cdot 1N$-solutions at 70° is of the order: trichloroacetate, 1; bromoacetate, 1·2; iodoacetate, 3·6; chloroacetate, 26; dichloroacetate, 120. It is remarkable that the iodoacetate is more stable than the bromoacetate, and that the dichloroacetate is so very stable compared with the mono- and tri-chloroacetates. J. C. W.

α- and β-**Cinenic Acids.** H. RUPE and A. BLECHSCHMIDT (*J. pr. Chem.*, 1917, [ii], **96**, 59—64).—α-Cinenic acid, when heated with dilute sulphuric acid, is converted into an isomeric liquid β-cinenic acid (Rupe and Altenburg, A., 1909, i, 7). The isomeric nature of the two acids is now confirmed by careful analysis of some of the salts of the β-acid (*silver* salt; *magnesium* salt, with $\frac{1}{2}H_2O$; *calcium* salt, with $2H_2O$), the results excluding the possibility of the β-acid being in reality a hydroxy-lactone. The action of hydrogen bromide in acetic acid solution converts both α- and β-cinenic acids into the same bromo-derivative (compare Rupe and Altenburg, *loc. cit.*), the β-isomeride undergoing the change more readily. As the bromo-product on treatment with magnesium carbonate and water yields cinogenic acid, which on distillation gives α-cinenic acid, it is possible to reconvert the β-acid into its α-isomeride. From these results, it appears highly probable that the α- and β-acids are of similar structure. D. F. T.

The Rôle of Atmospheric Oxygen and Alkali in the Oxidation of Acetone with Potassium Permanganate. Pyruvic Acid as an Intermediate Product. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1917, **39**, 2657—2671. Compare A., 1916, i, 372).—A study of the oxidation of acetone by potassium permanganate in the presence of varying amounts of potassium hydroxide. In the absence of alkali, acetone is not perceptibly oxidised by potassium permanganate at the ordinary temperature. In the presence of small amounts of alkali, the oxidation is incomplete, but in the presence of sufficient alkali the acetone is oxidised solely to acetic and oxalic acids and carbon dioxide in such a way that one molecule of carbon dioxide is formed for each molecule of acetic and oxalic acids, thus:

$$COMe_2 + 4O = CH_3 \cdot CO_2H + CO_2 + H_2O.$$
$$COMe_2 + 7O = C_2O_4H_2 + CO_2 + 2H_2O.$$

The proportion of oxalic acid increases gradually but continually with increasing alkalinity, indicating that the formation of oxalic acid is dependent on a molecular transformation that is catalysed by or dependent on the alkali. On the basis of Denis's work (compare A., 1907, i, 997) and the intermediate formation of pyruvic acid as shown by Fournier (compare A., 1908, i, 247), the author

gives the following series of changes for the oxidation of acetone by potassium permanganate in the presence of alkali,

$$COMe_2 \rightarrow CH_2{:}CMe{\cdot}OH \rightarrow HO{\cdot}CH_2{\cdot}CMe(OH)_2 \rightarrow CHO{\cdot}CMe(OH)_2 \rightarrow CO_2H{\cdot}CMe(OH)_2 \rightarrow$$

$$CH_3{\cdot}CO{\cdot}CO_2H \rightarrow CH_3{\cdot}CO_2H + CO_2$$

$$CH_3{\cdot}CO{\cdot}CO_2H \rightarrow CH_2{:}C(OH){\cdot}CO_2H \rightarrow C_2O_4H_2 + CO_2.$$

comparable with the formation of iodoform, as explained by Pieroni and Tonnioli (compare A., 1914, i, 6). The functions of the alkali in the oxidation are: (1) to give rise to the active enol, *iso*acetone; (2) to cause the enolisation of pyruvic acid; (3) to neutralise the acids formed, and thus prevent their further oxidation; (4) to determine the velocity of oxidation; and (5) to catalyse the absorption of atmospheric oxygen. W. G.

The Distillation of Cellulose and Starch in a Vacuum. AMÉ PICTET and J. SARASIN (*Compt. rend.*, 1918, **166**, 38—39).—When cellulose or starch is heated gradually under a pressure of 12—15 mm., the fraction distilling between 200° and 300° amounts to about 45 per cent. of the original, and consists of an oily, crystalline paste, from which crystals have been separated corresponding in properties with Tanret's *laevoglucosan*, $C_6H_{10}O_5$ (A., 1894, i, 564) (see, further, *J. Soc. Chem. Ind.*, 1918, **37**, Feb.). J. F. B.

Pine-wood Lignin. PETER KLASON (*Svensk. kem. Tidskrift*, 1917, **29**, 5—16, 47—52; from *Chem. Abstr.*, 1917, **11**, 2482—2483).—The lignin was obtained from sulphite waste by two procedures: (*a*) by saturating the waste liquors with calcium chloride, and (*b*) by adding to the filtered liquor naphthylamine hydrochloride. The sample (*a*) was purified as the barium salt and (*b*) as the calcium salt. These salts were analysed. The first lignin had a composition suggesting that it was composed of 1 mol. of coniferyl alcohol and 3 mols. of hydroxyconiferyl alcohol, $C_{40}H_{48}O_{15}$ (MeO, 11·55% found; 12·4% calc.). The second lignin (*b*) corresponds with 4 mols. of hydroxyconiferyl alcohol and 6 mols of trihydroxycinnamyl alcohol, $C_{84}H_{108}O_{40}$. Klason's conception of lignins is that they are formed by condensation of phenols with side-chains in positions 1, 3, 4, in a manner not unlike the proteins and dextrins. The sulphite process breaks up the larger molecules. Molecular weight determinations correspond with formulæ twice the size of the above. Coniferyl alcohol is always the chief component of native lignin, and this explains the formation of

$$C_6H_3Me(OMe){\cdot}OH,$$

$C_6H_3(C_2H_5)(OMe){\cdot}OH$, and $C_6H_3(C_3H_7)(OMe){\cdot}OH$ on destructive distillation of wood. Pure lignin and coniferyl alcohol both give several colour tests, but the latter only on keeping. Freshly prepared from an emulsion extracted with ether, it does not react. G. B.

Identity of Cyanuric Acid with so-called Tetracarbimide. E. H. WALTERS and LOUIS E. WISE (*J. Amer. Chem. Soc.*, 1917, **39**, 2472—2477).—Scholtz described a product obtained by the oxidation of uric acid by hydrogen peroxide in alkaline solutions as "tetracarbimide" (A., 1902, i, 140), and this has not been called into question until recently, when Venable and Moore suggested that the compound was really cyanuric acid (*J. Amer. Chem. Soc.*, 1917, **39**, 1750). The identity of the substance with cyanuric acid is now fully established, optically, titrimetrically (thymolphthalein as indicator), and by the characteristic copper salt.

In an application of Scholtz's method with slight modifications, a small amount of carbonyldicarbamide has been obtained from uric acid. It might be that this is an intermediate product between uric and cyanuric acids, for it readily loses ammouia, and so produces the latter acid.

Cyanuric acid has now been isolated from some eighteen different soils (compare A., 1917, i, 622). J. C. W.

Conversion of Methyleneaminoacetonitrile into Iminodiacetonitrile. J. R. BAILEY and H. L. LOCHTE (*J. Amer. Chem. Soc.*, 1917, **39**, 2443—2444).—Bailey and Snyder have reported that methyleneaminoacetonitrile unites directly with hydrogen cyanide to form iminodiacetonitrile, $NH(CH_2 \cdot CN)_2$ (A., 1915, i, 389). Delépine had previously stated that these compounds do not react together at all (*Bull. Soc. chim.*, 1903, [iii], **29**, 1202), and the present authors have now found that a catalyst is necessary. Pure hydrogen cyanide does not combine with methyleneaminoacetonitrile, but if a trace of hydrochloric acid is added to the mixture, the reaction proceeds quickly to completion. The original agent contained hydrochloric acid as a preservative.

J. C. W.

Hydrolysis of Sodium Cyanide. FREDERICK PALLISER WORLEY and VERE ROCHELLE BROWNE (T., 1917, **111**, 1057—1062). —The degree of hydrolysis is measured by passing a current of air through the sodium cyanide solution and absorbing the hydrogen cyanide from the issuing gas by means of a solution containing 0·2% of picric acid and 2% of sodium carbonate. This indicator solution is changed to a reddish-brown colour, which is matched against the colours produced when the same current of air is made to pass through aqueous solutions of hydrocyanic acid containing respectively slightly more and slightly less free acid than the solution of sodium cyanide under investigation. The strengths of the hydrocyanic acid solutions required are determined by preliminary tests. In the actual determination, the three flasks, to each of which is attached an absorption tube containing the same volume of indicator solution, are arranged in series, the sodium cyanide solution being in the middle.

The results obtained are in very satisfactory agreement with the mass law expressed by the equation [illegible]

which C is the molar concentration of the cyanide and P the percentage hydrolysis. The value of C was varied from 0·0073 to 5·2 mols. per litre. The influence of temperature on the hydrolysis is shown by the fact that $k \times 10^4$ increases from 0·135 at 0° to 0·484 at 25° and 0·72 at 30°. H. M. D.

The Action of Aluminium Chloride on Cymene. A. W. Schorger (*J. Amer. Chem. Soc.*, 1917, **39**, 2671—2679. Compare Boedtker and Halse, A., 1917, i, 124).—When cymene is heated with aluminium chloride at from 60—150°, the products are $\beta\gamma$-dimethylbutane, benzene, toluene, *m*-xylene, and 1-methyl-3:5-di*iso*propylbenzene. Small amounts of the catalyst favour the formation of toluene, whilst the formation of benzene increases with the amount of catalyst used.

1-*Methyl*-3:5-*di*iso*propylbenzene*, as isolated, has b. p. 215—218°, D^{20} 0·8668, n_D^{20} 1·4950, and on oxidation with nitric acid (D 1·15) yields uvitic (*s*-methyl*iso*phthalic) acid, giving a *dimethyl* ester, m. p. 98°. With chlorosulphonic acid, the hydrocarbon gave a thiochloride, which with ammonia yielded a *thioamide*, m. p. 92°. W. G.

Action of Benzenesulphonyl Chloride on Organic Bases in Anhydrous Ether. George L. Schwartz and William M. Dehn (*J. Amer. Chem. Soc.*, 1917, **39**, 2444—2453).—In continuation of Dehn's studies on the production of additive compounds of bases and haloids, especially acid chlorides, in anhydrous ether (A., 1912, i, 833; 1914, i, 1169; 1915, i, 954, etc.), the behaviour of benzenesulphonyl chloride has been investigated. As before, the reagents have been mixed in a large excess of ether, and any precipitates formed, immediately or after days or even months, have been analysed.

In harmony with previous results, it is found that (1) the initial reaction is additive, (2) the reactions are non-ionic, (3) and that light promotes reaction.

With primary and secondary amines, the additive product soon gives place to a greater or less extent to the hydrochloride of the base, thus, $C_6H_5{\cdot}SO_2Cl + RNH_2 = SO_2Ph{\cdot}RNH,HCl$, and this $= SO_2Ph{\cdot}RNH + HCl \longrightarrow RNH_2,HCl$. The benzenesulphonyl derivative of the base remains in solution. The secondary reactions are promoted by heat, traces of water, and by the free bases. Thus aniline, the toluidines, propylamine, hexylamine, benzidine, phenylhydrazine, carbamide, diethylamine, dipropylamine, di*iso*butylamine, di*iso*amylamine, methylaniline, ethylaniline, piperidine, and dibenzylamine give mixtures of the additive compound and the hydrochloride of the base. The appearance and analysis of the precipitates and the speed of the reactions are recorded. Phenylhydrazine and carbamide give precipitates which contain as much as 82% and 94% of the additive compounds respectively, but the other bases fall very short of this.

With tertiary bases, additive compounds of the types $B,C_6H_5 \cdot SO_2Cl$ and $B_2,C_6H_5 \cdot SO_2Cl$ are formed, but these may be contaminated by other salts if traces of moisture are not excluded, thus, $C_6H_5 \cdot SO_2Cl,B + H_2O \longrightarrow C_6H_5 \cdot SO_3H + B,HCl$, and, subsequently, $C_6H_5 \cdot SO_3H,B$. Tribenzylamine gives a *compound*, B_2X, microscopic prisms, m. p. 174—176°; tripropylamine yields a *compound*, BX, long needles, m. p. 52°; pyridine forms *compounds*, BX, microscopic prisms, m. p. 110—112°, and B_2X, large, rectangular plates; α-picoline gives a *compound*, B_2X; quinoline forms *compounds*, BX, needles, and B_2X, stout rhombs; quinaldine gives a mixture of mono- and di-derivatives; acridine gives a *compound*, B_2X, golden, prismatic needles, m. p. 192°; antipyrine forms a *compound*, BX, needles. J. C. W.

Dichloroamine T and Chlorinated Eucalyptol (D 1·2). ROBERT B. KRAUSS and EDWARD CREDE (*J. Amer. Chem. Soc.*, 1917, **39**, 2720—2722).—An improved method is given for the preparation of dichloroamine T [toluene-*p*-sulphodichloroamide] on a large scale, by which a stable product is obtained. When chlorine is passed into eucalyptol in good daylight at such a rate that the temperature does not exceed 80°, chlorinated oil (D 1·2) is obtained which can be used as a solvent for dichloroamine T for surgical purposes without requiring the addition of prepared paraffin oil as a diluent. By further chlorination of the oil (D 1·2), either directly at 100° or in boiling chloroform solution, an amber-coloured *oil* (D 1·4) is obtained of the consistency of molasses.

W. G.

Solubilities of Anthracene, Anthraquinone, *p*-Dibromobenzene, Phenanthrene, and Iodine in Various Solvents. JOEL H. HILDEBRAND, E. T. ELLEFSON, and C. W. BEEBE (*J. Amer. Chem. Soc.*, 1917, **39**, 2301—2302. Compare this vol., ii, 36).—The solubility of anthracene, anthraquinone, *p*-dibromobenzene, phenanthrene, and iodine has been determined at 25° in the solvents alcohol, benzene, carbon disulphide, carbon tetrachloride, ethyl ether, and hexane. In all cases except that of iodine, the amount dissolved was determined by evaporation of the solvent from a weighed portion of the saturated solution; in the case of iodine, the estimation was effected by titration with sodium thiosulphate solution. The following values, in grams of solute per 100 grams of solvent, were obtained: Alcohol solution: 0·328 anthracene, 0·437 anthraquinone, 10·35 *p*-dibromobenzene, 4·91 phenanthrene. Benzene solution: 1·86 anthracene, 83·8 *p*-dibromobenzene, 59·5 phenanthrene. Carbon disulphide solution: 2·58 anthracene, 90·0 *p*-dibromobenzene, 80·3 phenanthrene. Carbon tetrachloride solution: 0·732 anthracene, 36·6 *p*-dibromobenzene, 26·3 phenanthrene. Ethyl ether solution: 1·42 anthracene, 0·104 anthraquinone, 71·3 *p*-dibromobenzene, 42·9 phenanthrene. Hexane solution: 0·37 anthracene, 25·9 *p*-dibromobenzene, 9·15 phenanthrene, and 1·32 iodine. J. F. S.

Miscibility in the System Aniline-Water-Glycerol. I. M. Kolthoff (*Chem. Weekblad*, 1917, **14**, 1081—1089).—At 18°, glycerol of 89% strength is miscible with aniline in all proportions, a fact which affords a basis for a method of estimating the proportion of water in glycerol. A. J. W.

Acid and Basic Properties of Various Compounds. H. I. Waterman (*Chem. Weekblad*, 1917, **14**, 1126—1131).—An investigation of the alkali and acid equivalents of various substances, determined by the effect produced on the decomposition of monoses by sodium hydroxide, and the inversion of sucrose by hydrochloric acid. Sulphanilic acid has no basic character, and salicylic acid differs from its isomerides by displaying the properties of a monobasic acid. Structural formulæ to acount for these phenomena are suggested. A. J. W.

A Catalytic Decomposition of certain Phenol Silver Salts. II. Thermal Decompositions: The Formula of the Unpolymerised Residues. W. H. Hunter and F. E. Joyce (*J. Amer. Chem. Soc.*, 1917, **39**, 2640—2646. Compare A., 1916, i, 717).—When *p*-chlorophenol is brominated in glacial acetic acid solution, it yields 4-*chloro*-2:6-*dibromophenol*, needles, m. p. 92°, giving a *silver* salt, occurring in an orange and a white form. When this silver salt is boiled in benzene, it yields a white, amorphous solid which is a mixture of the two *compounds* $(C_6H_2OClBr)_n$ and $(C_6H_2OBr_2)_n$ in the proportion of 1:0·86. When the silver salt is treated with ethyl iodide in the cold, it gives these two compounds, together with some 4-*chloro*-2:6-*dibromophenetole*, m. p. 52·5°.

If *p*-chlorophenol is dissolved in an excess of aqueous potassium hydroxide, and to the solution is added a solution of potassium iodate and another of iodine in potassium hydroxide, on gradually acidifying this mixture, with continual shaking, 4-*chloro*-2:6-*di-iodophenol*, m. p. 107—108°, is obtained, giving a pale yellow *silver* salt. When boiled in benzene, the silver salt gives a mixture of the two *compounds* $(C_6H_2OClI)_n$ and $(C_6H_2OI_2)_n$ in the proportion of 1:0·61.

The *silver* salt of 2:6-dichloro-4-bromophenol is also decomposed by hot benzene, giving the two compounds $(C_6H_2OClBr)_n$ and $(C_6H_2OCl_2)_n$ in the proportion of 1:2·26.

In each of these cases it was found that the molecules of the silver salt split up, losing some of their halogen from the ortho-position and some from the para-position, the ratio varying widely between the different salts. There are slight indications that the halogen in the para-position is the more readily removed, and that the ease of removal of the halogens is in the descending order, iodine, bromine, chlorine.

By the decomposition of the silver salt of 4-chloro-2:6-dibromophenol by ethyl iodide, more of the molecules lost their halogen from the ortho-position than in the decomposition by hot benzene. W. G.

Basic Salts of the Metals of the Alkaline Earths. E. BELLONI and E. BACCI (*Gazzetta*, 1917, **47**, ii, 159—170).—The *compound*, $Ba_2(SO_3{\cdot}C_6H_4{\cdot}OH)_3{\cdot}OH,8H_2O$, is obtained in prismatic crystals when a warm dilute solution of phenolsulphonic acid is neutralised with barium hydroxide until it becomes alkaline to phenolphthalein. Of the eight molecules of water contained in this salt, four are lost when it is kept over sulphuric acid, three more at 130°, and the other only after prolonged heating at 170°. When a dilute solution of the salt is treated with carbon dioxide, barium carbonate is precipitated, and barium phenolsulphonate can be recovered from the solution.

The *compound*, $Ba_2(SO_3{\cdot}C_6H_4{\cdot}OH)_2(OH)_2,4H_2O$, is produced by boiling a solution of 20 grams of barium phenolsulphonate in 200 c.c. of water with 15 grams of barium hydroxide. It is a white powder, very slightly soluble in water. When this solution is treated with carbon dioxide, barium carbonate is precipitated, but the filtrate on concentration yields the monobasic phenolsulphonate first described.

The *compound*, $Ca_2(SO_3{\cdot}C_6H_4{\cdot}OH)_2(OH)_2,4H_2O$, is prepared by boiling a solution of phenolsulphonic acid with an excess of lime.

The *compound*, $Ba_3(CO_2{\cdot}C_6H_4{\cdot}OH)_2(OH)_4(OH_2)_2,4H_2O$, is obtained by pouring a solution of sodium salicylate (6 grams) and sodium hydroxide (1 gram) in 50 c.c. of water into a boiling solution of 6 grams of barium chloride in 50 c.c. of water.

The constitution of these and other basic salts of the metals of the alkaline earths is discussed, and formulæ are assigned to them derived from the theories of Werner. R. V. S.

The Substitution Products of the Aminophenols and of their Derivatives. WALTER FUCHS (*Monatsh.*, 1917, **38**, 331—341).—The knowledge of the relative effect of the amino- and hydroxyl radicles in the aminophenols in directing the position of entry of a new substituent into the nucleus is not complete, and the behaviour of *p*-aminophenol and its ortho-isomeride towards bromination has been examined. By the careful addition of a chloroform solution of bromine to *p*-aminophenol dissolved in a mixture of chloroform and ether, a green reaction product was obtained which, from the fact that on treatment with ethyl sulphate and alkali it yielded a quantity of 3:5-dibromo-4-aminophenetole, must have contained 3:5-dibromo-4-aminophenol; the two bromine atoms had therefore been directed into the two ortho-positions to the amino-group. *p*-Acetylaminophenol when treated with bromine in a similar manner gave rise to 2:6-dibromo-4-acetylaminophenol, the influence of the hydroxyl group predominating over that of the acetylamino-radicle; this product on ethylation gave 2:6-*dibromo-4-acetylamino-phenetidine*, $NHAc{\cdot}C_6H_2Br_2{\cdot}OEt$, needles, m. p. 198°. Attempts to brominate *o*-aminophenol proved less satisfactory, but it is possible that some 3:5-dibromo-2-aminophenol was formed. As a result of this and earlier investigations (Fuchs, A., 1915, i, 520;

Reverdin and Düring, A., 1899, i, 266; Hodurek, A., 1897, i, 276; Möhlau and Ohmichen, A., 1882, 395), the scheme

$$NH_2 > (OH,OAlk) > NHAc$$

may be given to represent the relative directing power of the groups towards a new substituent, the positions of the hydroxyl and alkyloxy-groups relative to one another remaining yet to be decided. D. F. T.

Molecular Rearrangements in the Camphor Series. XIII. The Decomposition Products of the Methyl Ester of *iso*Aminocamphonanic Acid. A New Reaction Involving the Formation of the Methyl Ether of a Hydroxy-acid. WILLIAM A. NOYES and GLENN S. SKINNER (*J. Amer. Chem. Soc.*, 1917, **39**, 2692—2718).—It has been shown in an earlier paper (A., 1913, i, 161) that *iso*aminocamphonanic acid is decomposed by nitrous acid, with the formation of *cis*-camphonolactone, an unsaturated acid, b. p. 150°/60 mm. (decomp.), and a saturated acid, which decomposes at 160°. The present work was undertaken with the object of studying the behaviour of the methyl ester of this acid towards nitrous acid.

A much better yield of *aβ*-methyl *l-iso*camphorate was obtained by doubling the amount of sulphuric acid previously used (*loc. cit.*) and reducing the time of heating to five hours. The following physical properties of the ester are given: b. p. 130°/8 mm., 138°/13 mm., 141·5°/16 mm., 144°/19 mm., 146°/22 mm.; $[\alpha]_D^{24.5}$ −65·5° and $[\alpha]_D^{22}$ −66·5° in 10·7% alcoholic solution.

β-Methyl *a-l-iso*camphoramate has m. p. 127—128° (corr.) and $[\alpha]_D^{28}$ −55·4° in 10% absolute alcoholic solution (compare *loc. cit.*). From this ester a much better yield of methyl *iso*aminocamphonanate by the method previously described is obtained if the heating is reduced to five minutes. The ester has b. p. 135—138°/10—12 mm.; $[\alpha]_D^{25}$ −49° and $[\alpha]_D^{25}$ −41·2° in 10·5% alcoholic solution. Its hydrochloride has m. p. 179—180° (corr.).

This hydrochloride when decomposed by nitrous acid yields at least six products, namely, the methyl ether and the methyl ester of *cis*-camphonolic acid, and the methyl esters of lauronolic acid, 1:2:2-trimethyl-Δ^4-*cyclo*pentene-1-carboxylic acid, *cis*-2-hydroxy-1:2:3-trimethyl*cyclo*pentane-1-carboxylic acid, and a secondary *β*-hydroxy-acid.

The *methyl ether* of cis-*camphonolic acid* has m. p. 87° (corr.), $[\alpha]_D^{28}$ +72·1°, gives *cis*-camphonolactone by treatment with hydrogen iodide, and can be synthesised by the action of methyl iodide on the silver salt of *cis*-camphonolic acid. It gives a *silver* salt and a *methyl* ester, m. p. 116—118°/28—29 mm., $[\alpha]_D^{22}$ +64·7° in 9% alcoholic solution.

1:2:2-*Trimethyl*-Δ^4-cyclo*pentene*-1-*carboxylic acid* has b. p. 135°/14 mm.; D_4^{20} 1·0132; D_4^{25} 1·0088; $[\alpha]_D^{23}$ +105·2 and in 10% alcoholic solution $[\alpha]_D^{25}$ +83·4°; n_C^{25} 1·47256; n_D^{25} 1·47560; n_F^{25} 1·48279; n_G^{25} 1·48887. The *methyl* ester has b. p. 75°/9 mm., 78·5°/15 mm.; $[\alpha]_D^{26.5}$ +76·6°. In 10% alcoholic solution it has $[\alpha]_D^{24}$ +74·4°; n_C^{25} 1·45454; n_D^{25} 1·45755;

n_F^{25} 1·46423; $n_{G'}^{25}$ 1·4697. The structure of this acid was proved by its oxidation to an inactive tribasic acid, which decomposed at its melting point, giving off carbon dioxide.

cis-2-*Hydroxy*-1:2:3-*trimethyl*cyclo*pentane*-1-*carboxylic acid* has m. p. 101—102°, $[\alpha]_D^{25}$ +35·6° in 7% alcoholic solution. It gives *sodium*, *calcium*, and *silver* salts. It is not oxidised by Beckmann's chromic acid mixture in the cold, and does not give a lactone by this treatment. It gives a comparatively stable, crystalline *iodide*, m. p. 85—87°, which when treated at once with sodium hydroxide yields lauronolic acid and no lactone. The *methyl* ester has b. p. 112—114°/18 mm.

The decomposition of the esters of aminocamphouanic and aminodihydrocampholytic acids by nitrous acid was also examined, but in neither case was an ether acid obtained. Methyl *d*-camphorate, b. p. 155°/25 mm., or 144°/15 mm., $[\alpha]_D^{20}$ +47·5°, gives β-methyl α-*d*-camphoramate, m. p. 154—155°, $[\alpha]_D^{25}$ +23·1° in 9·7% alcoholic solution, which yields methyl aminocamphonanate hydrochloride, m. p. 237°, $[\alpha]_D^{20}$ +26·2° in 10·7% alcoholic solution. This hydrochloride is decomposed by hydrochloric acid, giving a *methyl* ester, b. p. 78—85°/15 mm., $[\alpha]_D^{23\cdot5}$ +73·8° in 9·25% alcoholic solution, of an unsaturated *acid*, b. p. 125—130°/10 mm., $[\alpha]_D^{23\cdot5}$ +108·1°; D_4^{20} 1·0130. W. G.

Pyro-condensations in the Aromatic Series. III. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1917, **38**, 343—358. Compare A., 1917, i, 641).—Azobenzene vapour when heated strongly is liable to decompose suddenly. *p*-Toluidine when heated, readily underwent decomposition with formation of *pp'*-diaminodibenzyl and a little resinous matter, whereas *o*-toluidine was surprisingly resistant, yielding only a small quantity of anthracene and of uncrystallisable resins; benzonitrile also proved remarkably stable, and remained unaltered unless the temperature was raised so high as to cause complete decomposition. Phthalimide at 480° underwent rapid and almost quantitative conversion into benzonitrile, *iso*phthalimide probably occurring as an intermediate product. The presence of chlorine increases the stability of the phthalimide molecule, and whereas the decomposition of phthalimide was already appreciable at 350°, 4-chlorophthalimide formed *p*-chlorobenzonitrile only very slowly at 500°, whilst tetrachlorophthalimide, even at its temperature of carbonisation, in the neighbourhood of 600°, gave only sufficient nitrile to be detected by the odour.

The gradual thermal decomposition of benzoic acid gave rise to benzene, benzaldehyde, diphenyl, diphenyl-4-carboxylic acid, and a small quantity of diphenyl-4:4'-dicarboxylic acid; the formation of benzaldehyde is probably due to the reduction of benzoic acid by hydrogen already formed in the decomposition of part of the acid. Ethyl benzoate at a dull red heat was rapidly converted into the free acid and ethylene, but the methyl ester was much more stable and required a still higher temperature for its decomposition, then yielding benzene, diphenyl, methyl diphenyl-3-carboxylate and

diphenyl-4-carboxylate, and trioxymethylene; in a similar manner, the methyl group in toluene was retained by the benzene nucleus, and in ethylbenzene only the end carbon atom of the ethyl group suffered scission, the carbon atom adjacent to the benzene ring remaining attached to the latter. The great stability of methyl benzoate rendered it likely that in methyl toluate the ester grouping might prove more resistant than the methyl radicle, and this anticipation was realised, the product being methyl diphenylethane-4:4′-dicarboxylate, accompanied by a little *methyl stilbene*-4:4′-*dicarboxylate*, m. p. 226—227°, and trioxymethylene. Phenol was strikingly resistant, and after prolonged heating yielded only a small quantity of decomposition products, amongst which benzene and 4-hydroxydiphenyl were present; anisole suffered elimination of the methyl group with formation of phenol, but no trioxymethylene was observed. D. F. T.

Organic Additive Compounds of Potassium Hydroxide. WILLIAM M. DEHN and RUTH E. MERLING (*J. Amer. Chem. Soc.*, 1917, **39**, 2646—2657).—When benzoic acid and potassium hydroxide are brought together in anhydrous ether, the following successive additions and decompositions are recognised:

$$2Ph\cdot CO_2H + 2KOH \longrightarrow \underset{(I.)}{CPh(OH)_2\cdot O\cdot COPh} \longrightarrow$$
$$\underset{(II.)}{CPh(OH_2)\cdot O\cdot CPb(OH)\cdot OK} \longrightarrow \underset{(III.)}{2Ph\cdot CO_2K} + 2H_2O.$$

When benzoic anhydride is used in place of benzoic acid, the final salt (III) is the same as in the previous case, but an intermediate salt different from that (II) in the first case is formed,

$$COPh\cdot O\cdot COPh \longrightarrow COPh\cdot O\cdot CPh(OH)\cdot OK \longrightarrow$$
$$O[CPh(OH)\cdot OK]_2 \longrightarrow 2Ph\cdot CO_2K + 2H_2O.$$

A number of other acids were studied and salts were obtained, the molecular proportions of acid and potassium hydroxide reacting being either 2:1, or 1:1, or 1:2. All these salts, when first formed, were additive compounds, but later they might or might not yield the simple anhydrous salt. Initially, all the water was found to be present in the precipitate, and the progressive loss of water from the precipitate was studied in most cases. That the intermediate compounds were additive was also indicated by the fact that the final anhydrous salts did not take up a molecule of water from an ethereal solution of it. This formation of additive compounds with potassium hydroxide is not peculiar to organic acids, but is common to all organic compounds containing carbonyl groups. The types of compounds studied were acids, acid anhydrides, aldehydes, ketones, esters, amides, imides, alcohols and phenols, and certain miscellaneous compounds. A few oxygen-containing compounds, such as raffinose, saccharin, and camphor, failed to show any reaction with potassium hydroxide. W. G.

New Method of Preparing Aromatic Nitriles by Catalysis. ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 36—38).—When an ester of an organic acid is treated with ammonia, it is decomposed, yielding the alcohol and the amide of the acid, and the latter, on dehydration, gives the nitrile. The reactions may be effected simultaneously by passing the vapour of an ester of an aromatic acid, mixed with gaseous ammonia, over heated thoria at 450—470° (temperature measured in the channel supporting the catalysis tube). At the latter temperature the reaction is practically complete, and good yields of benzonitrile are obtained from methyl-, ethyl-, and *iso*propyl-benzoates. The liquid product of the reaction separates into two layers, the oily layer consisting almost entirely of benzonitrile, which is purified by rectification (b. p. 189—191°). Aldehydic products and gases consisting of hydrogen and olefines are derived from the alkyl group of the ester. The nitriles of *o*- and *p*-toluic acids may be prepared in exactly the same way, and phenylacetonitrile is obtained from ethyl phenylacetate. The method appears to be of general application and gives good yields. J. F. B.

Amides, Carbamido-compounds, and Carbamides containing an Aromatic Nucleus. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 2418—2443. Compare A., 1917, i, 552, 559, 695).—A large number of compounds of the above classes are described. These, and similar substances mentioned in the earlier papers, have been collected as intermediate material in another investigation, of which an early account is promised.

A. AMIDES. (a) *Amides of Substituted Benzoic Acids.*—3-*Amino-6-hydroxybenzamide* is best obtained by the action of aqueous ammonia at 110° on methyl aminosalicylate; it crystallises in silky needles, m. p. 194—197° (decomp.), and gives 3-*chloroacetylamino-6-hydroxybenzamide*, very pale purple platelets, m. p. 225—227°, when treated by the method already described (*loc. cit.*, 552). Six other amides of this series have been mentioned previously.

(b) *Amides of Aminophenylacetic Acids.*—*Methyl* m-*aminophenylacetate hydrochloride* crystallises in long, thin, glistening plates, m. p. 167—170° (decomp.); m-*aminophenylacetamide* forms transparent prisms, m. p. 164—166° (corr.); and m-*chloroacetylaminophenylacetamide* separates in prismatic needles, m. p. 187—188°. (For the parent acid and amides of the para-series, *loc. cit.*)

(c) *Derivatives of the Aminophenoxyacetamides.*—o-*Nitrophenoxyacetamide*, glistening needles, m. p. 194·5—195·5° (corr.), yields *o*-aminophenoxyacetic anhydride when treated with ferrous sulphate and ammonia. o-*Chloroacetylaminophenoxyacetic acid*,

$$CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

crystallises with $2H_2O$, which it loses at 110°/vac., and then melts at 144·5—145·5° (corr.); the acid *chloride* forms colourless plates, m. p. 52—59°, and the *amide* crystallises in needles, m. p.

158—161°. m-*Aminophenoxyacetamide*, from the ethyl ester, forms delicate, cream-coloured needles, m. p. 123·5—124° (corr.), and yields m-*chloroacetylaminophenoxyacetamide*, radiating masses of minute leaflets, m. p. 235—238° (decomp.). p-*Aminophenoxyacetamide* crystallises in creamy prisms, m. p. 127·5—128·5°, and the *chloroacetyl* compound separates in colourless needles, m. p. 195—196·5° (corr.), and forms a *hexamethylenetetraminium* salt, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NH_2,C_6H_{12}N_4$. p-*Nitrophenoxyacetyl chloride* crystallises in hexagonal tablets, m. p. 86—87° (corr.); p-*nitrophenoxyacetomethylamide* forms brilliant needles, m. p. 165·6° (corr.); and p-*aminophenoxyacetomethylamide*,

$$NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NHMe,$$

separates in creamy needles, m. p. 109·5—111° (corr.). The following 4-*aminophenoxyacetamides* are obtained from the corresponding esters: 2-*methyl-*, long, flat, glistening needles, m. p. 155·5—156° (corr.); 3-*methyl-*, very pale pink, filamentous masses, m. p. 136—137°; 2:5-*dimethyl-*, silky needles, m. p. 153—154° (corr.); 2-*methyl*-5-iso*propyl-*, diamond-shaped plates, m. p. 108—109° (corr.); 3-*methyl*-6-iso*propyl-*, pointed leaflets, m. p. 125—125·5° (corr.); 2-*bromo-*, masses of long, creamy needles, m. p. 159—160° (corr.); 6-*methoxy-*, glistening needles, m. p. 177·5—178·5° (corr.); 6-*carbethoxy-*, minute leaflets, m. p. 135—136° (corr.); 6-*acetyl-*, brownish-yellow leaflets, m. p. 138—139°. Colour reactions with ferric chloride and R-salt (after diazotisation) are described for most of these compounds. (For the parent acids or esters, *loc. cit.*)

(d) *Derivatives of Aminobenzenesulphonamides*.—Aniline-*m*-sulphonic acid is dissolved in an equivalent of *N*-sodium hydroxide, shaken with acetic anhydride, the solution evaporated under reduced pressure, and the sodium *m*-acetylaminobenzenesulphonate left is triturated with phosphorus pentachloride. The crude sulphonyl chloride so formed is treated with ammonia, and so converted into m-*acetylaminobenzenesulphonamide*, minute rhombs, m. p. 216—219°. This is hydrolysed by hydrochloric acid to the known *m*-aminobenzenesulphonamide, which forms a *chloroacetyl* compound, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$, aggregates of minute needles, m. p. 165° (clear). Sodium sulphanilate is acetylated in the same way, and finally converted into p-*chloroacetylaminobenzenesulphonamide*, needles, m. p. 215—217°.

B. CARBAMIDES. (a) *Carbamides of Substituted Benzoic Acids.*—*o*-Aminobenzoylcarbamide (*loc. cit.*) gives o-*chloroacetylaminobenzoylcarbamide*, long, glistening needles, m. p. 222—223° (decomp.), and *m*-aminobenzoylcarbamide yields the *chloroacetyl* compound, slender needles, decomp. 252—253°. p-*Nitrobenzoylcarbamide*, microscopic prisms, m. p. 243—246°, gives rise to p-*aminobenzoylcarbamide*, minute plates, partly decomposed, but not molten at 285°, and p-*chloroacetylaminobenzoylcarbamide*, decomp. 275—280°. o-*Hydroxybenzoylcarbamide* (*salicoylcarbamide*), microscopic, pale yellow crystals, m. p. 184—186° (decomp.), is obtained by the interaction of carbamide and *o*-acetoxybenzoyl

chloride in benzene, followed by agitation of the acetyl derivative with cold sodium hydroxide. m(?)-*Chloroacetylaminomethylbenzoylcarbamide*, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO\cdot NH\cdot CO\cdot NH_2$, a microcrystalline powder, m. p. 225—228° (decomp.), is obtained by the action of methylolchloroacetamide on benzoylcarbamide in sulphuric acid solution (compare Einhorn, A., 1906, i, 245).

(b) *Derivatives of Phenylacetylcarbamide.*—Phenylchloroacetyl chloride and carbamide yield *a-chlorophenylacetylcarbamide*, $CHPhCl\cdot CO\cdot NH\cdot CO\cdot NH_2$, needles, m. p. 198°. p-*Nitrophenylacetylcarbamide*, hair-like needles, m. p. 250—252° (decomp.), gives p-*aminophenylacetylcarbamide*, felted needles, m. p. 198—199° (evolution of gas), and p-*chloroacetylaminophenylacetylcarbamide*, m. p. 241° (decomp.).

(c) *Derivatives of Aminophenoxyacetylcarbamides.*—o-*Nitrophenoxyacetyl chloride*, long, silky, yellow needles, m. p. 41—42° (corr.), gives *o-nitrophenoxyacetylcarbamide*, cream-coloured, irregular prisms, m. p. 186—188°, which is easily hydrolysed, even by ammonia. p-*Nitrophenoxyacetylcarbamide*, m. p. 250° (decomp.), yields p-*aminophenoxyacetylcarbamide*, long needles, which melt at 198—199°, give off a gas, resolidify, and melt again, evolving gas, at above 240°, and p-*chloroacetylaminophenoxyacetylcarbamide*, minute, flat needles, m. p. 238—240° (decomp.). A better yield of this compound is obtained from the corresponding acid chloride and carbamide. p-*Chloroacetylaminophenoxyacetic acid*, from the aminophenoxyacetic acid, crystallises in rosettes of soft needles, with $1CH_3\cdot CO_2H$, m. p. 170° (free from solvent of crystallisation); the *chloride*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COCl$, forms aggregates of platelets, m. p. 147—152° (decomp.), and the *methyl* ester forms flat needles, m. p. 170—173°.

C. Aromatic Carbamides containing an Amido-group.—These carbamido-amides are generally prepared by the action of potassium cyanate on acetic acid solutions of the amino-amides. o-*Carbamidobenzamide*, $NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, crystallises in stout, cream-coloured, hexagonal plates, which melt at 184—185°, evolving ammonia, and changing thereby into solid benzoylenecarbamide; m-*carbamidobenzamide* forms flat needles, m. p. 235° (decomp.; resolidification), and gives m-*chloroacetylcarbamidobenzamide*, decomp. 223—224°. p-*Carbamidobenzamide* forms aggregates of prisms, m. p. 240—242° (gas evolved; resolidifies; continues to evolve gas; finally molten at 275°), and yields a *chloroacetyl* compound, hexagonal plates, decomp. 236—237°. m-*Carbamidophenylacetamide*, m. p. 201—202°, gives a *chloroacetyl* compound,

$$CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2,$$

very pale pink aggregates of platelets and needles, m. p. 179—181° (decomp.). p-*Carbamidophenylacetamide* forms rectangular plates, m. p. 233—236° (decomp.; resolidification), and gives a *chloroacetyl* compound, m. p. 200—201° (decomp.). p-*Carbamidophenoxyacetamide* crystallises in radiating masses of long, flat, pale brown needles, m. p. 230° (evolution of gas; resolidification; second m. p. 260°), and its *chloroacetyl* compound decomposes at 230°.

Methyl p-*carbamidophenoxyacetate*, m. p. 192—193°, gives a *chloroacetyl* compound,

$$CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2Me,$$

flat prisms, m. p. 181—183° (decomp.).

D. CARBAMIDES WITH OTHER SUBSTITUENTS AND SIDE CHAINS.—*p*-Hydroxyphenylcarbamide yields p-*chloroacetylcarbamidophenyl chloroacetate*, needles and long, thin plates, m. p. 185·5—187·5°, when boiled with chloroacetyl chloride and benzene; p-*acetylcarbamidophenyl acetate*, delicate, pale pink needles, m. p. 213·5—214° (corr.), when warmed with acetic anhydride and a little sulphuric acid; and p-*carbamidophenyl acetate*, m. p. 201—202·5°, when treated with acetyl chloride and pyridine. The latter may be chloroacetylated; p-*chloroacetylcarbamidophenyl acetate*,

$$CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot OAc,$$

forms spindles and plates, m. p. 181—182·5° (corr.).

p(?)-*Carbamidochloroacetylbenzylamine*,

$$NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl,$$

microscopic spears, m. p. 173—174°, is obtained by the action of methylolchloroacetamide on phenylcarbamide (Einhorn's method, *loc. cit.*).

p(?)-*Carbamidophenyl chloromethyl ketone*, creamy, nacreous plates, m. p. 197—198° (decomp.), is prepared by the condensation of phenylcarbamide and chloroacetyl chloride under the influence of aluminium chloride.

p-Acetylaminophenoxyethyl bromide is readily hydrolysed by hydrobromic acid to *β-bromoethoxyaniline hydrobromide*, thin plates, m. p. 227—228° (gas evolution). The free *base* (described as p-*aminophenoxyethyl bromide*) crystallises in minute, glistening platelets, m. p. 83—84·5°, decomp. 260°, and the crude salt reacts with potassium cyanate to give *β-bromoethoxyphenylcarbamide* (p-*carbamidophenoxyethyl bromide*), m. p. 160—162°. J. C. W.

The Behaviour of the Alkali Salts of the Polyhydroxybenzoic Acids at Higher Temperatures. DANICA MRAZEK (*Monatsh.*, 1917, **38**, 211—218).—The alkali salts of the dihydroxy- and trihydroxy-benzoic acids when heated at 200—300° do not undergo intramolecular rearrangement, and therefore do not behave like the potassium and thallium salts of salicylic acid, which give rise to the *p*-hydroxybenzoates, but resemble more closely the salicylates of sodium, lithium, and the alkaline earth metals, which undergo decomposition with formation of carbon dioxide and phenol. In an examination of the behaviour of the potassium salts of *a*- and *β*-resorcylic acids, protocatechuic acid, gentisic acid, gallic acid, and pyrogallolcarboxylic acid, it was found that carbon dioxide was generally liberated below 300°, whilst in the case of *β*-resorcylic acid, protocatechuic acid, and gallic acid a partial further substitution of carbon dioxide into the molecule, with formation of the corresponding polyhydroxyphthalic acid, was also observed. The lithium salt of *β*-resorcylic acid behaved similarly to the potassium salt, but with the sodium salt the formation of

dicarboxylic acid was negligible, and an amorphous *substance*, $C_{12}H_{10}O_3$, was obtained. With the sodium salt of protocatechuic acid no formation of a dicarboxylic acid was observable.

D. F. T.

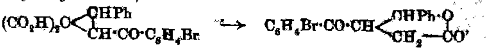
The *cyclo***Propane Series. III.** E. P. KOHLER, G. A. HILL, and L. A. BIGELOW (*J. Amer. Chem. Soc.*, 1917, **39**, 2405—2418. Compare A., 1917, i, 566—570).—In the earlier papers, three reactions of *cyclo*propane derivatives were described which involved rupture of the ring in the three possible ways, but the primary effect of some of the reagents could only be surmised. New compounds of this series have therefore been sought out in the hope of isolating from them definite products to fill the gaps in the chain of evidence, and a certain measure of success has been achieved.

Experiments with 3-p-*Bromobenzoyl-2-phenyl*cyclo*propane*-1 : 1-*dicarboxylic Acid*.—*p*-Bromophenyl styryl ketone condenses with the malonic esters under the influence of the sodium alkyloxides to give the *methyl* ester (needles, m. p. 96°) and *ethyl* ester (m. p. 75—76°) of γ-p-*bromobenzoyl-β-phenylethylmalonic acid*,

$$C_6H_4Br\cdot CO\cdot CH_2\cdot CHPh\cdot CH(CO_2H)_2,H_2O,$$

which crystallises in transparent plates. The methyl ester yields *methyl* γ-*bromo*-γ-p-*bromobenzoyl-β-phenylethylmalonate* on bromination; this exists in plates, m. p. 98°, and needles, m. p. 113°, which are separated after many crystallisations from methyl alcohol. The condensation of this compound to *methyl* 3-p-*bromobenzoyl-2-phenyl*cyclo*propane*-1 : 1-*dicarboxylate* proceeds smoothly. Two forms are produced; with magnesium methoxide, both bromo-compounds yield a product which crystallises in thin plates, m. p. 104°, whilst with potassium acetate and boiling methyl alcohol, both bromides give an isomeride which separates in compact tablets, m. p. 113°; the former is converted into the latter by boiling with methyl alcohol and a trace of an acid.

As usual with these compounds, the ring is opened between 1 and 3 by treatment with zinc dust and acetic acid, the product being the above methyl ester, m. p. 96°. Similarly, alkaline agents effect hydrolysis and also open the ring between 1 and 2. With sodium alkyloxides in moist ether, however, it is possible to control hydrolysis so that the *methyl hydrogen* ester (plates, m. p. 175—176°) and *ethyl hydrogen* ester (small tablets, m. p. 144°; the diethyl ester is not described) are produced. The ethyl hydrogen ester is the best material for the final hydrolysis, by the ordinary methods, to the free acid, and it may be prepared from the original ketone and ethyl malonate in a day or so without purifying the intermediate products. 3-p-*Bromobenzoyl-2-phenyl*cyclo*propane*-1 : 1-*dicarboxylic acid* crystallises with $1H_2O$ or $1Et_2O$, and changes on heating at 160—180° into *β*-p-*bromobenzoyl*-γ-*phenylbutyrolactone*,



which crystallises in needles, m. p. 116°, together with a trace of *a-benzylidene-γ-p-bromophenylcrotonolactone*, lemon-yellow plates, m. p. 180—183°. The butyrolactone is converted into *β-p-bromobenzoyl-γ-phenylisocrotonic acid*, CHPh:C(CO·C_6H_4Br)·CH_2·CO_2H, m. p. 156°, when shaken with just sufficient sodium methoxide in ether. This unsaturated acid yields *methyl γ-bromo-β-p-bromobenzoyl-γ-phenylbutyrate*, CHPhBr·CH(CO·C_6H_4Br)·CH_2·CO_2Me, m. p. 140° (decomp.), when esterified by means of hydrobromic acid; the same ester is also obtained by similar treatment of the butyrolactone. The substituted *iso*crotonic acid also gives benzaldehyde and *β-p-bromobenzoylpropionic* acid, thin plates, m. p. 140°, when treated with alkalis, so these are the products if the butyrolactone is left in contact with alkaline agents in excess.

3-*p*-Bromobenzoyl-2-phenyl*cyclo*propane-1:1-dicarboxylic acid also reacts with hydrogen bromide in acetic acid, yielding *γ-bromo-β-p-bromobenzoyl-γ-phenylethylmalonic acid*,

CHPhBr·CH(CO·C_6H_4Br)·CH(CO_2H)$_2$,

which separates in stout needles, and crystallises from ether in lustrous plates containing combined solvent. This acid suffers loss of hydrogen bromide when shaken with magnesium acetate in dry ether, with the formation of *a-carboxy-β-p-bromobenzoyl-γ-phenylbutyrolactone*, O<(CO——CH·CO_2H)(CHPh·CH·CO·C_6H_4Br),H_2O, in small, flattened needles, which readily change on heating into the above butyrolactone, m. p. 116°. The *methyl* ester, plates, m. p. 104°, is easily obtained from the *cyclo*propane acid directly. A small quantity of *β-bromo-β-phenyl-β′-p-bromobenzoyldimethylmalonic acid*,

CHPhBr·C(CO_2H)$_2$·CH_2·CO·C_6H_4Br,

is also formed by the action of hydrogen bromide on the *cyclo*propane acid. It crystallises in plates.

When the *cyclo*propane acid methyl ester is left with magnesium methoxide, the ring is ruptured between 1 and 2, and *methyl β-p-bromobenzoyl-γ-phenylvinylmalonate*,

CHPh:C(CO·C_6H_4Br)·CH(CO_2Me)$_2$,

is formed; this crystallises in needles, m. p. 104°, which change into a stereoisomeride (hard, lustrous prisms, m. p. 92—93°) when left with hydrochloric acid.

*Experiments with Benzoyl-m-nitrophenyl*cyclo*propanedicarboxylic Acid.*—*m*-Nitrostyryl phenyl ketone and the malonic esters react to form *methyl γ-benzoyl-β-m-nitrophenylethylmalonate*, short needles with ½MeOH, m. p. 92°, or silky needles, m. p. 102°, and the *ethyl* ester, m. p. 100—100·5°. These yield the corresponding *γ-bromo*-esters, COPh·CHBr·CH(C_6H_4·NO_2)·CH(CO_2R)$_2$; each exists in two forms, the methyl ester in long, silky needles, m. p. 149·5°, and short, lustrous needles, m. p. 129·3°; the ethyl ester in short, brittle needles, m. p. 101°, and soft, slender needles or hard prisms, m. p. 98·5°. These bromo-esters are condensed to *cyclo*propane derivatives by the usual mild agents, as above. The following esters are mentioned: *methyl 3-benzoyl-2-m-nitrophenyl-*

cyclo*propane*-1 : 1-*dicarboxylate*, stable, large, prismatic plates, m. p. 109·3°, and labile, slender needles, m. p. 111·5°; the *methyl hydrogen* ester, short, hard prisms, m. p. 154·5°; and the *ethyl* ester, small plates, m. p. 67°. The methyl hydrogen ester is hydrolysed by the prolonged action of alcoholic potassium hydroxide to 3-*benzoyl*-2-m-*nitrophenyl*cyclo*propane*-1 : 1-*dicarboxylic acid* (I), which crystallises with $1H_2O$ in lustrous plates, and decomposes at above 135° into α-m-*nitrobenzylidene*-γ-*phenylcrotonolactone* (II),

$$\text{(I)}\quad (CO_2H)_2C{<}\genfrac{}{}{0pt}{}{CH\cdot C_6H_4\cdot NO_2}{CHBz} \qquad \text{(II)}\quad NO_2\cdot C_6H_4\cdot CH{:}C{<}\genfrac{}{}{0pt}{}{CH{:}CPh}{CO{-}O},$$

small, yellow plates, m. p. 208°, and β-*benzoyl*-β-m-*nitrobenzylidenepropionic acid*, $NO_2\cdot C_6H_4\cdot CH{:}CBz\cdot CH_2\cdot CO_2H$, slender needles, m. p. 172°. Syntheses of these products are also described.

The *cyclo*propane methyl ester, m. p. 109·5°, yields *methyl* β-*benzoyl*-β-m-*nitrobenzylidenemethylmalonate*,

$$NO_2\cdot C_6H_4\cdot CH{:}CBz\cdot CH(CO_2Me)_2,$$

prisms, m. p. 139·5°, when boiled for a long time with magnesium methoxide solution; this ester gives *m*-nitrobenzoic acid when oxidised with permanganate in aqueous acetone, but a compound, m. p. 197°, of undetermined structure is formed in dry acetone.

J. C. W.

4 : 4′-Dimethylbenzophenone and its Condensation with Phenol. M. Gomberg and J. D. Todd (*J. Amer. Chem. Soc.*, 1917, **39**, 2392—2396).—Toluene and carbon tetrachloride condense under the influence of aluminium chloride to give a mixture of ditolylmethylene dichlorides, which suffer violent decomposition when distillation is attempted. On hydrolysis, the mixture gives a 30—35% yield of di-*p*-tolyl ketone, m. p. 93°, and an oily residue of other tolophenones, soluble in light petroleum. The pure ketone reacts with phosphorus pentachloride at 100° to form di-*p*-tolylmethylene dichloride, as a mobile, green liquid, which decomposes at above 175°. This behaves like diphenylmethylene dichloride towards phenol (A., 1916, i, 29), giving diphenoxydi-*p*-tolylmethane, m. p. 132—133°, if the agents are diluted with benzene, or p-*hydroxyphenyldi*-p-*tolylcarbinol* if no diluent is used. Two forms of this carbinol are described, but no suitable medium for crystallisation has been found. The *benzenoid* form,

$$OH\cdot C_6H_4\cdot C(C_6H_4Me)_2\cdot OH,$$

obtained by precipitation with carbon dioxide from a solution in sodium hydroxide, is pale yellow, turns red aud melts at about 70°, and evolves water at 125°; the *quinonoid* form,

$$(OH)_2{:}C_6H_4{:}C(C_6H_4Me)_2,$$

obtained by pouring an acetic acid solution into water, is orange-red, becomes dark red and melts at about 65°, and freely gives off water at above 90°.

J. C. W.

The Action of Phosphorus Trichloride on Unsaturated Ketones. James B. Conant (*J. Amer. Chem. Soc.*, 1917, **39**, 2679—2684).—Phosphorus trichloride reacts with αβ-unsaturated ketones in glacial acetic acid solution, and on diluting the products

with water, β-ketonic phosphonic acids are obtained. It is best to allow the reaction mixture to remain overnight before diluting it with water. In this way, phenyl *p*-methoxystyryl ketone yields *β-benzoyl-α-4-methoxyphenylethylphosphonic acid*,

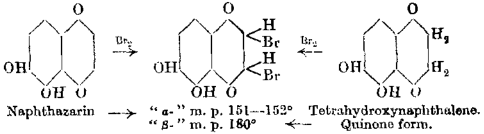
$$OMe{\cdot}C_6H_4{\cdot}CH(PO_3H_2){\cdot}CH_2{\cdot}COPh,$$

m. p. 189°, giving an *oxime*, m. p. 156° (decomp.), a crystalline *sodium* salt, soluble *calcium* and *barium* salts, and insoluble *silver* and *lead* salts. Phenyl styryl ketone yields *β-benzoyl-α-phenylethylphosphonic acid*, m. p. 116°, and distyryl ketone yields *β-cinnamoyl-α-phenylethylphosphonic acid*,

$$PO_3H_2{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CHPh.$$

W. G.

Bromohydroxynaphthaquinones. A. S. WHEELER and V. C. EDWARDS (*J. Amer. Chem. Soc.*, 1917, **39**, 2460—2468. Compare A., 1916, i, 392).—1:4:5:6-Tetrahydroxynaphthalene is an interesting compound, since it appears to exist in only one form, but reacts sometimes as a tetrahydric phenol and sometimes as a quinone. The bromination of the compound, and also of its oxidation product, naphthazarin, in the cold has now revealed another curious type of isomerism. Both substances yield quinone dibromides, thus:



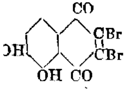
but the two products are not identical and not interchangeable, although they are isomeric and yield the same derivatives on treatment with alcohol, which removes the elements of hydrogen bromide. It may be that in one, both bromine atoms are outside the ring and the hydrogen atoms within, whilst in the other form a different spatial arrangement is observed.

Naphthazarin reacts with bromine in cold chloroform to give the "α"-form of 5:6-*dihydroxy*-1:4-*naphthaquinone* 2:3-*dibromide*, crystallising in lemon-yellow prisms, which become red and then grey between 135° and 150°, and have m. p. 151—152°. This loses hydrogen bromide when warmed with alcohol, giving 2(or 3)-*bromo*-5:6-*dihydroxy*-1:4-*naphthaquinone*, in reddish-brown prisms, m. p. 188—189° (after giving a coloured vapour at 170°), and yields the tetrahydroxynaphthalene on reduction with stannous chloride. It also forms a *diacetate*, $C_{14}H_{10}O_4Br_2$, when boiled for a long time with acetyl chloride. This crystallises in colourless plates, which turn red at 110° and melt at 166—167°, and also become deep red when kept, and it reacts with alcohol to form the *diacetate* of the monobromo-compound, bright yellow, silky needles, m. p. 191—192°, which may be obtained also by direct acetylation.

Naphthazarin yields 5:6-diacetoxy-1:4-naphthaquinone, m. p. 189—190°, when boiled with acetyl chloride, but the tetra-acetoxynaphthalene, m. p. 277—279°, is formed if acetic anhydride is applied (compare Zincke and Schmidt, A., 1895, i, 613). The diacetate yields 1:4-*dihydroxy*-5:6-*diacetoxynaphthalene* on reduction with stannous chloride; this forms colourless, microscopic plates, which turn red at 230° and have m. p. 241—243°.

Tetrahydroxynaphthalene reacts with bromine in cold acetic acid to form the "*β*"-*modification* of 5:6-dihydroxy-1:4-naphthaquinone 2:3-dibromide. This crystallises in lemon-yellow prisms, which begin to turn red at 140° and have m. p. 180°. It loses hydrogen bromide in the sunlight, becoming steely-blue, and it yields all the products described above in connexion with the α-isomeride.

If tetrahydroxynaphthalene is brominated in acetic acid at 70°, the product is 2:3-*dibromo*-5:6-*dihydroxy*-1:4-*naphthaquinone* (annexed formula); this crystallises in red leaflets, m. p. 258°, and yields a 5:6-*diacetate*, yellow needles, m. p. 200—201°, which may be reduced to 2:3-*dibromo*-1:4-*dihydroxy*-5:6-*diacetoxynaphthalene*, colourless needles, m. p. 196—197°, by means of stannous chloride.



The many inter-reactions which have been established among these compounds are illustrated by a chart of formulæ.

J. C. W.

Oil of Artemisia Annua. K. Asahina and Yoshitomi (*J. Pharm. Soc. Japan*, 1917, 424, 1; *Perf. Ess. Oil Rec.*, 1917, **8**, 353—354).—Oil of *Artemisia annua* was freed from aldehydic constituents, distilled with steam, and fractionated. The lower fractions contained cineole and the higher *l*-camphor. The fraction boiling between 181° and 190°/10 mm. contained a new *ketone*, $C_{10}H_{16}O$, b. p. 182°, D_4^{14} 0·8906, $n^{18.5}$ 1·4695, mol. refraction 47·57 (calc., 47·45), yielding a *semicarbazone*, m. p. 95—96°. Reduction by means of hydrogen in presence of platinum converted the ketone into *tetrahydro-artemisia ketone*, $C_{10}H_{20}O$, b. p. 73°/15 mm., 173°/760 mm., $D_4^{19.5}$ 0·8262, n_D 1·42425, yielding a *semicarbazone*, m. p. 134—135°. (See also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.)

T. F. B.

Constituents of Formosan Lemongrass Oil. Kinzo Kafaku (*J. Chem. Ind. Tōkyō*, 1917, **20**, 825—833).—Formosan lemongrass oil contains an olefinic terpene which yields dihydromyrcene and 2:6-dimethyloctane on treatment with hydrogen under different conditions, and succinic and oxalic acids on oxidation; it is therefore believed to be myrcene. The oil also contains an aldehydic substance other than citral, which, however, has not been isolated. (See also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.)

T. F. B.

Action of Alkyl Nitrites on Pyrrole. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 127—131).—The action of ethyl nitrite on pyrrole in the presence of sodium ethoxide at 5—10° results in the production of nitrosopyrrole-black (A., 1917, i, 413) and the *ethyl* ester of the *oxime* of *maleinimide*,

$$\begin{matrix} OH\cdot N{:}C-NH \\ CH{:}CH \end{matrix} > CO,$$

which forms colourless needles, m. p. about 100°. This compound is hydrolysed by water, acids, or alkalis with formation of the *oxime*, $C_4H_4O_2N_2$, which decomposes at 195° and melts at 205°. The oxime forms a *sodium* salt, $C_4H_3O_2N_2Na$, which when treated with ethyl iodide yields a derivative isomeric with the ethyl ester above described; it crystallises in pale yellow needles, m. p. 55—60°. The oxime of maleinimide when treated with bromine yields fumaric acid and monobromomaleinimide. R. V. S.

Betaines and Alkyliodides. R. VON WALTHER and ALBERT B. WEINHAGEN (*J. pr. Chem.*, 1917, [ii], **96**, 50—58).—α-Chlorophenylacetic acid reacts normally with quinoline, giving rise to a betaine additive *compound* of the formula $C_{17}H_{14}O_2NCl$ (*mercurichloride*, m. p. 140°; *perchlorate*, decomp. at 120°), but with pyridine, α-picoline, and nicotine the additive process is complicated by the liberation of carbon dioxide, the products respectively being benzylpyridinium chloride, *benzylpicolinium chloride* (*aurichloride*, m. p. 133—134°; *platinichloride*, m. p. 212—213°; *dichromate*, m. p. 129°), and *benzylnicotinium chloride*, decomp. at 236° (*diaurichloride*, decomp. at 178°; *picrate*, decomp. at 99°). With quinaldine and *s*-collidine, however, no additive product is obtained, probably owing to steric hindrance, but the latter base, presumably on account of its greater basicity, extracts hydrogen chloride from the chlorophenylacetic acid. Pyridine and α-chloropropionic acid when heated together give rise to ethylpyridinium chloride (*aurichloride*, m. p. 190° decomp.), carbon dioxide being liberated. With benzyl chloride and nicotine, the monobenzyl- or dibenzyl-nicotinium compound is obtained according to the proportions taken; *dibenzylnicotinium diaurichloride* decomposes at 183° and the *platinichloride* at 211°, whilst the picrate has m. p. 122°.

With *o*-nitrobenzyl chloride, the following products were obtained: *o-Nitrobenzylpyridinium chloride*, $C_{12}H_{11}O_2N_2Cl,1\frac{1}{2}H_2O$, colourless needles, m. p. 103°; *mercurichloride*, leaflets, m. p. 145°; *dichromate*, m. p. 172°; *perchlorate*, with $1H_2O$, m. p. 154°; *platinichloride*, m. p. 223°, decomp. at 228°; *picrate*, needles, m. p. 148°. *o-Nitrobenzyl-α-picolinium chloride*, $C_{13}H_{13}O_2N_2Cl$, m. p. 115°; *aurichloride*, m. p. 132—133°. *o-Nitrobenzylquinolinium chloride*; *dichromate*, carbonises at 190—200°; *mercurichloride*. *o-Nitrobenzylnicotinium chloride*; *platinichloride*, $C_{17}H_{21}O_2N_3PtCl_6$, m. p. 227—229°; *diaurichloride*; *dichromate*, m. p. 110°. No reaction was observable between *o*-nitrobenzyl chloride and collidine,

probably on account of steric hindrance. *m*-Nitrobenzyl chloride in a similar manner was made to yield m-*nitrobenzylpyridinium chloride*, crystalline spangles with $1\frac{1}{2}H_2O$, m. p. 97—99° (*mercurichloride*, needles, m. p. 117—119°; *dichromate*, m. p. 189° decomp.; *perchlorate*, needles, m. p. 142°; *picrate*, needles, m. p. 142°; *platinichloride*, m. p. 213—215°); m-*nitrobenzyl-α-picolinium chloride*, needles, m. p. 118° (*aurichloride*, m. p. 159°); m-*nitrobenzylquinolinium chloride* (*dichromate*, carbonises at 190°; *mercurichloride*); and m-*nitrobenzylnicotinium chloride* (*platinichloride*, m. p. 204—205° decomp.; *aurichloride*, m. p. 185° decomp.). Similarly, *p*-nitrobenzyl chloride yielded p-*nitrobenzylpyridinium chloride*, with $1\frac{1}{2}H_2O$, m. p. 64—66° (*mercurichloride*, needles or tablets, m. p. 137°; *perchlorate*, needles, m. p. 131°; *dichromate*; *picrate*, needles, m. p. 171°; *platinichloride*, spangles, m. p. 210—211°); p-*nitrobenzylnicotinium chloride* (*aurichloride*, decomp. near 80°; *platinichloride*, m. p. 223°); p-*nitrobenzyl-α-picolinium chloride* (*aurichloride*, m. p. 159°; *platinichloride*, needles, m. p. 217°; *mercurichloride*, needles, m. p. 139—140°); and p-*nitrobenzylquinolinium chloride* (*dichromate*, m. p. 176°; *mercurichloride*); 2-methylquinoline and collidine did not form additive compounds with *p*-nitrobenzyl chloride.

Collidine (*perchlorate*, m. p. 233°) when heated with benzaldehyde gives rise to *benzylidenecollidine*, an undistillable oil (*mercurichloride*, m. p. 226°; *platinichloride*, with $1H_2O$, m. p. 236—238°), but no reaction was observable with acetaldehyde, nitrobenzaldehyde, or chloral.

Attempts to prepare alkylaminoacetic acids by the decomposition of pyridinebetaine with the aid of nitric acid or of hydriodic acid and phosphorus were unsuccessful, the only isolated product being pyridine. D. F. T.

The Esterification of 2:4-Lutidinetricarboxylic Acid. ALFRED KIRPAL and KARL REIMANN (*Monatsh.*, 1917, **38**, 249—265. See A., 1906, i, 697; 1907, i, 722).—When 2:4-dimethylpyridine-3:5:6-tricarboxylic acid (2:4-lutidinetricarboxylic acid) is esterified by means of alcohol and hydrogen chloride, the sole product is the 6-*ethyl* ester, $C_{12}H_{13}O_6N,2H_2O$, colourless prisms, m. p. 100°, to the formation of which there is least steric hindrance; the constitution of this ester is demonstrated by conversion through the corresponding *amide*, $C_{10}H_{10}O_5N_2$, m. p. 240° (decomp.), into 6-*amino*-2:4-*dimethylpyridine*-3:5-*dicarboxylic acid*, $C_9H_{10}O_4N_2$, m. p. 242° (decomp.), which on treatment with nitrous acid and heating yields successively 6-*hydroxy*-2:4-*dimethylpyridine*-3:5-*dicarboxylic acid*, $C_9H_9O_5N,H_2O$, needles, m. p. 232°, and 6-hydroxy-2:4-dimethylpyridine (γ-lutidostyril; Hantzsch, A., 1885, 397). If the dimethylpyridinetricarboxylic acid is esterified with alcohol only, the above ester is obtained, together with a small quantity of the isomeric 5-*ethyl* ester, $C_{12}H_{13}O_6N,2H_2O$, colourless prisms, m. p. 80°, and then at 170° (decomp.), the two esters being also obtainable by the action of alcohol on the *anhydride*, rhombic tablets

m. p. 232° (decomp.), which was produced by heating the dimethylpyridinetricarboxylic acid with acetic anhydride. The 6-ethyl ester, unlike the 5-ethyl isomeride, is rapidly hydrolysed by boiling with water, and is inert towards alcoholic hydrogen chloride, whereas the latter ester is converted into the 5:6-*diethyl* ester,

$$C_{14}H_{17}O_6N,H_2O,$$

short prisms, m. p. 107°. By heating the ammonium salt of 2:4-dimethylpyridinetricarboxylic acid at 160—170°, it is possible to obtain the *imide*, $C_{10}H_8O_4N_2,H_2O$, m. p. above 300° (decomp.), which when heated in neutral aqueous solution gives the isomeric 5-amide and 6-amide in almost equal quantities.

The electrical conductivity of the 5-ethyl, 6-ethyl, and 5:6-diethyl esters, and of the parent 2:4-dimethylpyridinetricarboxylic acid, was examined in aqueous solution; the acid is a stronger electrolyte than pyridine-2:3:4:5-tetracarboxylic acid. D. F. T.

Two New Bases from Coal Tar. ALFRED ECKERT and SOPHIE LORIA (*Monatsh.*, 1917, **38**, 225—247).—Weidel and Pick (A., 1885, 556) isolated from bone oil a base which they believed to be 4-methyl-2-ethylpyridine, but the properties of this base when synthesised from γ-picoline and ethyl iodide prove that the base from bone oil was at any rate not pure, and possibly contained no ethyl-substituted pyridine whatever.

Examination of the collidine fraction obtained from coal tar revealed the presence of *s*-trimethylpyridine, 3:5-dimethylpyridine, a small quantity of a collidine, b. p. 165—168°, and of a base giving a picrate, m. p. 114—116°, together with 2:3:6-*trimethylpyridine* and 2:3:4-trimethylpyridine. These two bases have not been found previously in coal tar; the latter has already been produced synthetically (Guareschi, A., 1900, i, 568), whilst the former is now described for the first time. No indication of the presence of any ethyl derivative of pyridine was observed.

2:3:6-*Trimethylpyridine*, $C_5H_2NMe_3$, b. p. 173—174°/734 mm., forms a *platinichloride*, with $1H_2O$, m. p. 250—252° (decomp.), *aurichloride*, needles, m. p. 106°, *picrate*, yellow needles, m. p. 143—144°, and on oxidation yields *pyridine*-2:3:6-*tricarboxylic acid*, $C_5H_2N(CO_2H)_3,2H_2O$, m. p. approx. 130°, which at a higher temperature undergoes decomposition into pyridine-2:5-dicarboxylic acid.

2-Methyl-4-ethylpyridine, prepared by the action of ethyl iodide on α-picoline, was found to have b. p. 177—179°/751 mm. (Schultz, A., 1888, 64, gives 169—174°), and to give a platinichloride, yellow cubes, m. p. 203°, and a *picrate*, m. p. 141—142°, whilst the isomeric 2-methyl-6-ethylpyridine obtained in the same reaction had b. p. 160°/747 mm., gave a platinichloride, m. p. 188—190° (decomp.), and a *stannichloride*, m. p. 206—207°; synthetic 4-*methyl*-2-*ethylpyridine*, b. p. 173—175°/748 mm., yielded a *platinichloride*, m. p. 230°, a *picrate*, m. p. 115—116°, and a *mercurichloride*, m. p. 94—96°. D. F. T.

A New Synthesis of 2:4-Dioxythiazole and of its 3-Phenyl Derivative. RUDOLPH ANDREASCH (*Monatsh.*, 1917, 38, 203—209. Compare Andreasch, A., 1880, 877; Andreasch and Zipser, A., 1903, i, 855).—When potassium cyanate is added to a cold aqueous solution of equimolecular quantities of thiolacetic and acetic acids, the potassium salt of carbamylthiolacetic acid, $NH_2\cdot CO\cdot S\cdot CH_2\cdot CO_2H$, is produced; on repeated recrystallisation from hot water, this acid undergoes dehydration into 2:4-dioxythiazole, $S<\begin{matrix}CO-NH\\ CH_2\cdot CO\end{matrix}$. Phenylcarbimide and thiolacetic acid in ethereal solution react readily, with formation of 2:4-dioxy-3-phenylthiazole, $S<\begin{matrix}CO-NPh\\ CH_2\cdot CO\end{matrix}$, and carbanilide, the formation of the latter being due to the action of water on the phenylcarbimide.

The observed conversion of 3-phenyl*iso*thiohydantoin into 3:4-dioxy-3-phenylthiazole, carbamylthiolacetic acid, thiolacetic acid, and aniline under the influence of mineral acids is probably due to the decomposition following two different courses, one involving mere elimination of the imino-group and the other depending on the disruption of the cyclic molecule; however, the possibility that the phenyl*iso*thiohydantoin contained some of the 2-phenyl isomeride is not excluded. D. F. T.

Reduction of 4-Anisylidenehydantoin-1-acetic Acid and its Ethyl Ester. DOROTHY A. HAHN and C. PAULINE BURT [with TREAT B. JOHNSON] (*J. Amer. Chem. Soc.*, 1917, **39**, 2468—2472. Compare A., 1917, i, 475).—A variety of products is formed when this acid is reduced with sodium amalgam. Using one equivalent proportion of 2% amalgam and aqueous alcohol as the solvent, and boiling for one hour, keeping the mixture neutral by additions of acetic acid, *sodium* 4-*anisylidenehydantoin*-1-*acetate* separates in well-defined, greenish-yellow plates, which become white on dehydration. After boiling for two hours, the salt which separates on cooling in needles is *sodium* 4-*anisylhydantoin*-1-*acetate*, whilst after boiling with an excess of amalgam, the *disodium* salt, $CO_2Na\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CO_2Na)\cdot CH_2\cdot C_6H_4\cdot OMe$, is obtained as a crystalline precipitate, which gives the corresponding open-chain acid (*loc. cit.*) on acidifying with hydrochloric acid.

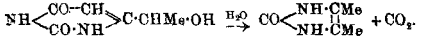
Reduction with zinc and aqueous acetic acid gives a small amount of a *zinc* salt of the formula,

$$\begin{matrix} & NH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot O \\ OMe\cdot C_6H_4\cdot CH:C\cdot CO\cdot O & \text{———————} Zn \end{matrix}$$

This yields the original 4-anisylidenehydantoin-1-acetic acid on acidifying.

These salts do not melt below 315°, and when they were encountered in the earlier work they were erroneously regarded as a geometric isomeride of the parent acid. J. C. W.

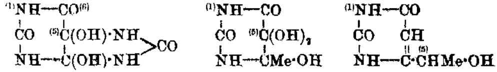
Pyrimidines. LXXXVI. Production of Glyoxalones by Hydrolysis of Pyrimidine Nucleosides. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2396—2405. Compare A., 1916, i, 754; 1917, i, 585, 667).—In recent papers, it has been shown that certain hydroxypyrimidine compounds can be converted into glyoxalones merely by hydrolysis with acids; thus, the secondary uracil-nucleoside, 4-α-hydroxyethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, yields 4 : 5-dimethylglyoxalone,



This remarkable reaction presents, therefore, the expulsion of a carbon atom from a 6-membered ring, with the formation of a 5-membered nucleus.

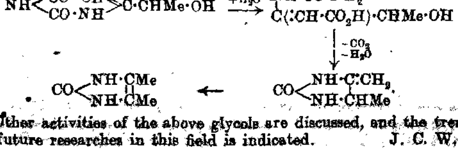
Somewhat analogous reactions of the pyrimidine ring have been known for a long time, but these are the result of oxidation and not mere hydrolysis. Thus, the oxidation in alkaline media of uric acid to allantoin, and of 4-methyluracil to parabanic acid, represent such a removal of a carbon atom. In both cases, the accepted interpretation of the reaction is that given by Behrend, who supposes that the glycols are first produced by oxidation and that subsequent rearrangements take place within these molecules.

Between these glycols and the uracil-nucleosides there is just one feature in common, namely, a hydroxyl group five places removed from the nitrogen atom numbered 1; thus:



Uric acid glycol. Trihydroxydihydromethyluracil. Secondary uracil-nucleoside.

Should the union between the nitrogen atom 1 and carbon atom 6 be broken, for example, by hydrolysis, there would be a hydroxyl group available for a recondensation to a 5-membered ring, and this is the explanation offered of the glyoxalone formation. The following scheme illustrates the probable course of the change:



Other activities of the above glycols are discussed, and the trend of future researches in this field is indicated. J. C. W.

The Decomposition of the Three Ethoxyphenylhydrazines by Hydrochloric Acid. HARTWIG FRANZEN and MORITZ SCHMIDT (*J. pr. Chem.*, 1917, [ii], **96**, 1—25).—It is already known that in

the aminophenylhydrazines the presence of the amino-group reduces the stability of the linking between the two nitrogen atoms (Franzen and von Fürst, A., 1914, i, 206; 1917, i, 58, 59), and the results of the present investigation demonstrate that the ethoxy-radicle exerts a similar but less powerful influence.

p-Ethoxyphenylhydrazine was obtained by Altschul's method; the hydrochloride when pure has m. p. 165° (decomp.); the base yields a *benzylidene* derivative, $C_{15}H_{16}ON_2$, rose-red needles, m. p. 124—125°; a pyruvic acid *derivative*, $OEt\cdot C_6H_4\cdot NH\cdot N:CMe\cdot CO_2H$, yellow needles, m. p. 118°; and a *dibenzoyl* derivative, $C_{22}H_{20}O_3N_2$, colourless needles, m. p. 146°. *o-Ethoxyphenylhydrazine*,

$$OEt\cdot C_6H_4\cdot NH\cdot NH_2,$$

was prepared by converting *o*-phenetidine into *sodium o-ethoxydiazobenzenesulphonate*, $OEt\cdot C_6H_4\cdot N_2\cdot SO_3Na$, yellow crystals, decomp. with mild explosion at 170°, and reducing this with zinc dust and acetic acid to *sodium o-ethoxyphenylhydrazinesulphonate*, $OEt\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3Na$, colourless, pearly leaflets, m. p. 205° (decomp.), which on decomposition with aqueous-alcoholic hydrochloric acid gave the *hydrochloride*, needles, m. p. 159—160° (decomp.), of the desired base; *benzylidene* derivative, $C_{18}H_{18}ON_2$, pale yellow needles, m. p. 98—99°; pyruvic acid *derivative*, $OEt\cdot C_6H_4\cdot NH\cdot N:CMe\cdot CO_2H$, yellow needles, m. p. 138°; *dibenzoyl* derivative, colourless crystals, m. p. 158°. *m*-Phenetidine, prepared from *m*-nitroaniline by way of *m*-nitrophenol and *m*-nitrophenetole, was, by successive diazotisation and reduction, converted into *m-ethoxyphenylhydrazine*, $OEt\cdot C_6H_4\cdot NH\cdot NH_2$; *hydrochloride*, colourless; *benzylidene* derivative, colourless needles, m. p. 80°.

When heated with boiling 2*N*-hydrochloric acid, *o*-ethoxyphenylhydrazine hydrochloride undergoes decomposition with formation of *p*-phenetidine, phenetole, *p*-azophenetole, ethyl chloride, ammonia, and nitrogen, and analogous products, with the exception of the azo-compound, were observed in the decomposition of the ortho-isomeride. The decomposition in each case probably involves a primary formation of chloroamine or of ethoxyphenylchloroamine produced by the reactions $OEt\cdot C_6H_4\cdot NH\cdot NH_2 + HCl = OEt\cdot C_6H_4\cdot NH_2 + NH_2Cl$ and $OEt\cdot C_6H_4\cdot NH\cdot NH_2 + HCl = OEt\cdot C_6H_4\cdot NHCl + NH_3$ respectively, the various isolated products resulting from the subsequent reactions of these primary products. By allowing the action of hydrochloric acid on these ethoxyphenylhydrazines to occur in the presence of a reducing agent such as stannous chloride, the above concurrent reactions become replaced by the single reaction $OEt\cdot C_6H_4\cdot NH\cdot NH_2 + 2H = OEt\cdot C_6H_4\cdot NH_2 + NH_3$, so that the quantity of ammonia formed supplies a convenient measure of the relative rates of the reaction with the ortho-, meta-, and para-compounds. By proceeding in this manner, it is shown that *p*-ethoxyphenylhydrazine is reduced most rapidly and the meta-isomeride least rapidly, so that the weakening effect of the ethoxy-group in various positions on the stability of the N–N linking falls in the order $p > o > m$, although the influence of the ethoxy-group is much less than that of the amino-group.

The decomposition of the three phenetidines by boiling hydrochloric acid, with formation of ethyl chloride, was also investigated, with the result that the reaction was found to occur most rapidly with *p*-phenetidine and least rapidly with *o*-phenetidine.

D. F. T.

The Nitrogen Distribution in Protalbic and Lysalbic Acids. CORNELIA KENNEDY and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1917, **39**, 2734—2736).—Lysalbic and protalbic acids have been prepared from egg-albumin by Paal's method (compare A., 1902, i, 653), and their nitrogen distributions have been determined by Van Slyke's method and compared with that of the original albumin, with the following results:

	Percentages in		
	Egg-albumin.	Protalbic acid.	Lysalbic acid.
Ammonia nitrogen	9·08	5·08	8·21
Humin ,,	4·71	4·00	4·49
Cystine ,,	0·72	0·11	0·51
Arginine ,,	6·05	6·32	6·23
Histidine ,,	6·48	7·96	6·42
Lysine ,,	10·09	13·73	12·50
Amino-nitrogen in filtrate from bases	61·26	58·17	58·37
Non-amino-nitrogen in filtrate from bases	4·58	5·22	2·70
Total	102·97	100·59	94·43

W. G.

Animal Globulin. I—VI. Confirmed and not Confirmed. JOHANNES STARKE (*Zeitsch. Biol.*, 1917, **68**, 147—159. Compare A., 1901, i, 242).—The author points out that his views on globulin, based on experiments with ovoglobulin, have since been confirmed by Hekma's work on fibrinogen (A., 1916, i, 513). He also claims priority for the demonstration of the transformation of albumin into globulin, usually ascribed to Moll (A., 1904, i, 356; but see Bywaters and Tasker, A., 1913, i, 1399). H. W. B.

The Effect of Prolonged Acid Hydrolysis on the Nitrogen Distribution of Fibrin with Especial Reference to the Ammonia Fraction. ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1917, **39**, 2736—2745).—Fibrin was hydrolysed by boiling with 20% hydrochloric acid for periods of time ranging from one hour to six weeks, and the distribution of nitrogen in the products was determined by Van Slyke's method. The figures for ammonia nitrogen in an acid hydrolysate include not only the amide nitrogen in the protein molecule, but also some ammonia derived from the deamination of certain of the amino-acids. The extent of this deamination depends on the length of hydrolysis, the monoamino-acids being deaminised much more easily than the histone bases. Cystine is not the only amino-acid which undergoes deamination when boiled with hydrochloric acid (com-

pare Van Slyke, A., 1912, i, 735). The figures, in a Van Slyke analysis, for histidine, arginine, and lysine are not appreciably altered by a hydrolysis extending over six weeks, providing that all tryptophan has been so altered that it is not precipitated on the addition of phosphotungstic acid. Increases in the insoluble humin nitrogen owing to prolonged hydrolysis are probably due to carbonisation. W. G.

Origin of the Humin Formed by the Acid Hydrolysis of Proteins. III. Hydrolysis in the Presence of Aldehydes. II. Hydrolysis in the Presence of Formaldehyde. Ross Aiken Gortner and George E. Holm (*J. Amer. Chem. Soc.*, 1917, **39**, 2477—2501. Compare A., 1915, i, 726; 1916, i, 681).—The nitrogen distribution in the hydrolysates of fibrin and gelatin, obtained by boiling these proteins with hydrochloric acid and varying quantities of trioxymethylene, has been determined by Van Slyke's methods, with the modification that the humin fraction has been differentiated into (*a*) "acid-insoluble" humin, (*b*) "acid-soluble" humin, precipitated by calcium hydroxide, and (*c*) "phosphotungstate" humin, precipitated by phosphotungstic acid.

With fibrin, the addition of aldehyde increases the yield of black, insoluble humin up to a maximum, about 100% above the normal. Further quantities of aldehyde then cause a decrease in the amount of insoluble humin and an increase in the soluble humin up to a second maximum, when the continued addition of aldehyde causes decreases in the humin fractions and an increase in ammonia. With gelatin, formaldehyde has no influence on the humin fraction, which is very small, but causes a steady increase in the yield of ammonia. This difference between the two proteins is obviously to be connected with the lack of cystine, histidine, tyrosine, and tryptophan in gelatin. With which of these amino-acids the humin formation is connected can therefore be ascertained by hydrolysing mixtures of gelatin and these acids in the presence of formaldehyde. Cystine and histidine are not the critical acids. Tyrosine causes no increase in insoluble humin, but a considerable increase in soluble humin, which is not the true humin of protein hydrolysis, as it is not black but reddish-yellow. Tryptophan, however, is the all-important constituent. If this is added to gelatin, the hydrolysates correspond with those obtained from fibrin.

As tryptophan does not give rise to humin when boiled with hydrochloric acid unless an aldehyde is present, the inference is that an aldehydic substance, as yet unknown, is produced during protein hydrolysis, but not in sufficient quantity to combine with all the tryptophan, since added aldehyde gives a higher yield of humin. Indole, alone, also yields humin when boiled with hydrochloric acid and formaldehyde, so the condensation does not involve the side chain in the case of tryptophan. Pyrrole also produces humin, but not so pyridine, which suggests that whilst the pyrrole ring is critical, it is possibly not the imino-group which is connected with the condensation. That the α-amino-group of trypto-

phan remains intact in the humin is proved by the fact that the humin formed from tryptophan and trioxymethylene under the most favourable conditions contains half its nitrogen in the amino-condition, just as in the free acid. Most probably, therefore, it is position 2 of the indole complex which is concerned in humin formation.

Further experiments on mixtures of the pure amino-acids are well in hand, but the authors are already convinced that tryptophan and some aldehydic component of the protein molecule are the only factors involved, and they adversely criticise Roxas's results in the same field (A., 1916, i, 797). J. C. W.

Helicorubin. I, II. Ch. Dhéré and G. Vegezzi (*J. Physiol. Path. gén.*, 1917, **17**, 44—52, 53—67. Compare A., 1917, i, 421).—The bile of the snail *Helix pomatia* contains a dialysable red pigment, helicorubin (Krukenberg, = enterohæmatin of MacMunn), and a non-dialysable, brown pigment, for which the name *helicofuscin* is suggested by the present authors. By means of acidified alcohol, helicorubin is transformed into hæmatin, spectrometrically identical with the substance obtained from vertebrate hæmoglobin. Potassium permanganate changes helicorubin into the same pigment with absorption band in the yellow as is obtained from hæmatin, and, finally, sodium hyposulphite reduces helicohæmatin to hæmatoporphyrin (of vertebrates). The bile was obtained from hibernating snails, free from chlorophyll.

These experiments show helicorubin to be an "embryonic or ancestral" form of hæmoglobin, as was already surmised by Sorby and by MacMunn. G. B.

"Carbohydrate" Group of the True Nucleic Acids. II. R. Feulgen (*Zeitsch. physiol. Chem.*, 1917, **100**, 241—258. Compare A., 1914, i, 1098).—The elementary analysis of sodium nucleate prepared from the thymus indicates the empirical formula

$$C_{43}H_{47}O_{25}N_{15}P_4Na_4$$

for the substance. A study of the hydrolytic products shows, however, that if the carbohydrate groups present in the molecule consist of dextrose, the molecular weight of sodium nucleate must be considerably larger than that indicated by the above formula. The author finds that, as a matter of fact, the carbohydrate groups consist of glucal (compare Fischer, A., 1914, i, 252) instead of dextrose molecules, the chief reactions of glucal being given by the carbohydrate isolated from the hydrolytic products of the nucleate. The assumption of glucal ($C_6H_{10}O_4$) instead of dextrose ($C_6H_{12}O_6$) molecules also stands in harmony with the above empirical formula. H. W. B.

The Rennetic Properties of Pepsin. Howard T. Graber (*J. Ind. Eng. Chem.*, 1917, **9**, 1125—1126).—In comparative estimations of the rennetic activity of calf rennet and of pepsin from the hog's stomach, it was found that whereas the former never failed

to coagulate fresh milk or to give comparable results when diluted, the latter usually failed to coagulate fresh milk and did not show an activity proportional to its dilution. The pepsin was most active in milk of an acidity of 0·2% or more, whilst the activity of the rennin was not promoted by such high concentration of acid. By bringing the acidity of fresh milk to 0·185% by the addition of lactic acid, the results were comparable with those produced in fresh milk by the rennet. These results support the view that the two enzymic activities of pepsin are associated in a single molecule, and that on contact with milk and acid, or protein and acid, coagulation of the milk or hydrolysis of the protein is effected (see also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.). C. A. M.

Some Nitrogenous Auxoamylases. ELBERT W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1917, **39**, 2745—2752).—An examination of the effect of various nitrogenous substances on the hydrolytic activity of the amylases of the saliva on starch, those which increase the activity being called auxoamylases. α-Amino-acids, whether aliphatic or cyclic, act as auxoamylases, this being true in the case of cyclic compounds whether the amino-group is in a side chain, as in tyrosine, or in the ring, as in the aminobenzoic acids. The position of the amino-group in the benzene ring with reference to the carboxyl group has no effect on the activity. Not only do the acid amides not act as auxoamylases, but the entry of an amino-group in the carboxyl group destroys the effect of an amino-group elsewhere in the molecule. Thus aspartic acid is an auxoamylase, asparagine is not. The sulphonyl group, if substituted for the carboxyl group in an amino-acid, destroys the stimulating effect of the amino-group on the amylases. Replacement of one of the hydrogen atoms in an amino-group by an acyl group, as in hippuric acid, does not destroy its stimulating action. Imides, however, are not auxoamylases. The proteins act as auxoamylases towards ptyalin, the effect increasing as the number of free amino-groups increases by the hydrolysis of the protein. As far as the tests go, they indicate that amino-acids act as auxoamylases not only on ptyalin, but also on the pancreatic amylase. W. G.

Supposed Action of Potassium Permanganate with Plant Peroxydases. H. H. BUNZELL and H. HASSELBRING (*Bot. Gaz.*, 1917, **63**, 225—228; from *Physiol. Abstr.*, 1917, **2**, 544).—Permanganate, reduced to a brown solution by excess of various organic substances, can still oxidise guaiacum, pyrogallol, or potassium iodide, and on the basis of these experiments the authors criticise the conclusion drawn by Reed (compare A., 1917, i, 423, 424), when he observed this phenomenon with horse-radish extract, that a specific interaction of peroxydase with permanganate was taking place to give a high-grade oxygenating substance. G. B.

Physiological Chemistry.

The Chemistry of the Proteins. I. The Protein Fractions of Blood-plasma. II. The Theory of the Agglutination of Bacteria. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, **83**, 228—243).—I. The theory is put forward that the various protein fractions of the plasma, such as fibrinogen, globulin, albumins, etc., are not chemical individuals, but form a series of which the individual members can pass one into another. The more complex proteins are assumed to be liberated from the cells in a state of low aggregation, with comparatively small amounts of adsorbed simple substances to keep them in a colloidally dispersed state, from which they can be readily flocculated by salts, etc. In the course of time, the state of aggregation is finer and the amount of adsorbed substances is increased, and the proteins are not then so readily precipitated. By alteration in the state of aggregation and amount of adsorbed simpler substances, variations in the physical properties can be produced, and a blood protein can thus be varied in its properties so as to pass from a readily aggregating substance like fibrinogen through a globulin to an albumose. Experiments which are stated to substantiate this theory are quoted.

II. Bacteria are supposed to act like colloidal solutions of certain proteins, which can be precipitated by neutral salts, weak acids, etc., and are changed in their properties as regards aggregation by adsorption of various substances from sera containing anti-substances. In this respect, the theory of the authors does not differ markedly from that of others. It differs, however, in that they do not lay so much stress on the effect of electrical discharge on the flocculation as on the effect of various adsorbed simpler substances on the capacity of the bacteria for holding water. The optimal conditions for flocculation often coincide with the point of electrical discharge, because at this point the solubility of the adsorbed substances in water is smallest. S. B. S.

Rate of Formation of Fibrin Ferment from Prothrombin by the Action of Thrombokinase and Calcium Chloride. JOHN MELLANBY (*J. Physiol.*, 1917, **51**, 396—403).—The formation of fibrin ferment proceeds in a manner similar to that observed in the activation of trypsinogen by enterokinase (Mellanby and Woolley, A., 1913, i, 113, 662); in both cases the velocity of the change is small at the outset, but the reaction proceeds with a constantly increasing acceleration. It is suggested hypothetically that the ultimate agent in the activation is the calcium ion, which does not act on pure prothrombin, but on prothrombin which has adsorbed thrombokinase, for the reaction is accelerated both by an increase in the calcium concentration and by an increase in the thrombokinase. G. B.

Metabolism of Arginine. IV. Effect on the Secretion of Total Creatinine. W. H. THOMPSON (*J. Physiol.*, 1917, **51**, 347—376. Compare A., 1917, i, 673).—Whereas arginine alone, given hypodermically to dogs, is converted into creatinine only to the extent of 4·5%, the addition of methyl citrate brings about a 7% conversion. When the substances are given by the mouth, there is no increased methylation of the guanidine nucleus, or when methyl benzoate replaces methyl citrate in the hypodermic experiments. Small hypodermic doses of guanidine carbonate gave an increase in the creatinine output up to 10·8% of the guanidine injected. G. B.

Oxydones. L. LOPEZ-PÉREZ (*Compt. rend. Soc. Biol.*, 1917, **80**, 326—327).—The oxydones of Batelli and Stern (which these authors consider responsible for the respiration of animal tissues and the oxidation of citric, fumaric, malic, and succinic acids, and of *p*-phenylenediamine) are not attacked by erepsin or by nuclease or takadiastase, so that the oxydones are not albumoses or peptones, or nucleic acid, or polysaccharides. G. B.

Changes in the Chemistry of the Brain as a Result of Intoxications. J. E. ABELOUS and L. C. SOULA (*J. Physiol. Path. gén.*, 1917, **17**, 157—170).—Rabbits were poisoned non-fatally by crystalloids (strychnine, cocaine, chloroform) and colloids (serum-albumin, egg-albumin, urohypotensin), and twenty to thirty-five days afterwards their brains were analysed by determining the protein nitrogen, amino-nitrogen (formol titration) protein phosphorus, lipoid phosphorus, etc. This affords a measure of the fission of proteins and lipoids in the brain; the degree of fission is considerably increased as compared with normal controls. The brain, the organ of psychical memory, also has a "chemical memory" of previous intoxications. The bearing of this on anaphylaxis is considered. G. B.

Power of Perfumes and their Solubility in Water and in Oil. E. LOUIS BACKMAN (*J. Physiol. Path. gén.*, 1917, **17**, 1—4. Compare A., 1917, i, 498).—In order that a substance may be odorous, it must be sufficiently soluble both in water and in lipoids, since the cells of the receptor organ for smell are covered with a watery fluid, whilst they themselves contain lipoid granules. Thus, the odours of the series of homologous alcohols first increase as the molecular weight rises, and then decrease again. The lower ones are comparatively odourless because little soluble in fats, cetyl alcohol because little soluble in water. Butyl alcohol, soluble in water and fats, has a powerful odour. The same applies to benzene, toluene, xylene, and ψ-cumene, and to isomeric butyl and amyl alcohols; also to the three nitrophenols and nitrotoluidines, to the dimethyltoluidines, bromoanilines, naphthylamines, etc. The changed solubility in water and in oil also explains why the introduction of an acetyl group renders alcohol odorous and aniline inodorous.

The Imbibition of Water by Muscular Tissue, with Special Reference to the Action of Caffeine. ALEXANDER BELÁK (*Biochem. Zeitsch.*, 1917, **83**, 165—217).—The rate of imbibition of various frogs' muscles was determined. The first stage is rapid increase in the water content of the tissue, which is regarded as an osmotic phenomenon, produced by the osmotic pressure of the inner contents of the tissue. The first stage is followed by a loss of water, due to a diffusion outwards of the salts, which process is accelerated by an increase of the permeability of the membranes. The third stage of the action of water is the ordinary imbibition by colloids which follows the laws of colloidal chemistry. The action of caffeine consists apparently, in the first instance, in causing an increase in the permeability by water, followed by a transient increase in the capacity for binding water. The toxic action consists in the coagulation of the proteins, which leads to a release of water by the tissues. S. B. S.

What Substance is the Source of the Light of the Firefly? E. N. HARVEY (*Science*, 1917, **46**, 241—243; from *Physiol. Abstr.*, 1917, **2**, 460. Compare A., 1917, i, 365—366, where in the second abstract photophlein should be photophelein).—Evidence is presented for the following conception. A colloid (photogenin) is oxidised and made to emit light under the influence of a thermostable dialysable substance (photophelein). The latter is cytolytic in its nature, and encourages oxidation by disintegrating the colloid aggregates and multiplying their surface relations. [Compare also Goss, *J. Biol. Chem.*, 1917, **31**, 271; Harvey, *ibid.*, 311.] G. B.

Saturated Hydrocarbons in Basking-shark Liver Oil. MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1917, **9**, 1098—1099).—The liver-oil of the basking-shark, *Cetorhinus maximus*, contains 41·92 to 55·51% of unsaponifiable matter, of which the unsaturated hydrocarbon *squalene* (Tsujimoto, A., 1916, i, 786) is a constituent (compare Chapman, T., 1917, **56**, 111). On distillation under a pressure of 5 mm. of the unsaponifiable matter from one specimen of the oil, 10% of a yellow liquid distilled between 170° and 190°, whilst at 244—260°, squalene (25%) distilled. The first fraction was washed with sodium hydroxide solution, and then distilled at 160—166° under 13 mm. pressure. It was a colourless, mobile liquid, which did not solidify when cooled below 0°. It had D_4^{15} 0·8768, refractive index n_D^{20} 1·4398, and iodine value 4·4. It began to boil at about 294° under 766 mm. pressure, and distilled almost completely at 296°. Its elementary composition (C = 84·39; H = 15·02%) and molecular weight (mean, 259) corresponded most closely with the formula $C_{18}H_{38}$. Since, however, normal octadecane is solid at the ordinary temperature, this hydrocarbon is probably an *iso*octadecane, and its low boiling point may be due to this cause. The specific refraction (n^2 formula) was 0·3283, and the molecular refraction 83·4. This hydrocarbon or mixture of hydro-

carbons was not present in two other specimens of the oil (see also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.). C. A. M.

Erepsin in Normal Urine and its Relation to other Proteases. S. G. Hedin and Y. Masai (*Zeitsch. physiol. Chem.*, 1917, **100**, 263—303).—The urine contains an enzyme which is capable of breaking down peptone and similar protein substances in alkaline solutions. It is isolated by saturating the urine with ammonium sulphate, dissolving the precipitate in water, and then dialysing until free from sulphate. The enzyme prepared in this way from human urine can sometimes digest caseinogen and some other proteins. It is suggested that this exalted ereptic action may be due to a true erepsin or, more probably, to a mixture of erepsin with another proteolytic enzyme.

Other proteolytic enzymes are also found in normal urine, namely, enzymes which effect the degradation of serum globulin and fibrin. They act best in an alkaline medium; and the above proteins, with the co-operation of the urinary erepsin, may be completely degraded to amino-acids. The effect of the co-operative action of the proteolytic and ereptic enzymes is considerably greater than the sum of the effects produced by the two enzymes working separately. The exalted proteolysis is observed, no matter whether the co-operating erepsin has been obtained from the urine, the intestinal wall, or from yeast cells. H. W. B.

Fat Content of Human Gall-stones. E. Salkowski (*Zeitsch. physiol. Chem.*, 1917, **100**, 259—262).—The specimen of human gall-stones examined was free from fat, but contained a resinous substance resembling fat in its solubility in ether and other solvents (compare A., 1917, i, 716). H. W. B.

The Relation between Chemical Constitution and Physiological Action. Frank Lee Pyman (T., 1917, **111**, 1103—1128).—A lecture delivered before the Chemical Society on December 6th, 1917. H. M. D.

Chemistry of Vegetable Physiology and Agriculture.

Effects of Oxygen and Carbon Dioxide on Nitrification and Ammonification. J. K. Plummer (*Cornell Univ. Agr. Expt. Stat.*, 1916, *Bull.* 384, 305—330; *Physiol. Abstr.*, 1917, **2**, 569).—Nitrification takes place in sealed flasks as long as there is a supply of oxygen; the optimum amount is 35—60%. Carbon dioxide is produced when lime is used; ammonium sulphate without lime causes only a slight increase in nitrification. If oxygen is present, carbon dioxide has no material effect. Under anaerobic

conditions, denitrification sets in, until all nitrates are destroyed. There is no optimum content of oxygen for ammonia production, but in its absence somewhat less is produced. G. B.

Influence of the Chemical Structure of the Compounds to be Ammonified on the Rate of Ammonification. K. MIYAKE (*J. Amer. Chem. Soc.*, 1917, **39**, 2378—2382).—An investigation on the relationship between the structure of organic nitrogen compounds and the rate at which they are converted into ammonia in the soil. Quantities of 100 grams of various air-dried soils were mixed respectively with 100 c.c. of water and quantities of leucine, tyrosine, acetanilide, benzanilide, acetamide, and benzamide containing 100 milligrams of nitrogen. The mixtures were allowed to incubate for periods of two, seven, twelve, and sixteen days, and the amount of ammonia formed was estimated. The rate at which the conversion into ammonia took place followed the order: acetamide > leucine > tyrosine > benzamide > acetanilide > benzanilide. It is shown that aliphatic nitrogen compounds are more rapidly converted into ammonia than aromatic compounds and aromatic amino-compounds more rapidly than aromatic imino-compounds under the conditions of the experiment. J. F. S.

Assimilation of Lactic Acid by Yeasts, and the Production of Pyruvic Acid by Yeasts and Oidia. P. MAZÉ and M. RUOT (*Compt. rend. Soc. biol.*, 1917, **80**, 336—339. Compare A., 1917, i, 310).—Yeasts grown in a confined atmosphere in a solution containing mineral salts and 2% of calcium lactate give about a 50% yield of pyruvic acid. By means of gas analyses and of the calcium carbonate formed, it is shown that the respiratory quotient is the same as that of the controls without lactate (about 0·7), which may indicate that the yeast burned proteins and possible traces of fat; the combustion of carbohydrate reserves would give a quotient equal to 1. The culture fluids contained also a small quantity of succinic and acetic acids, but no alcohol or aldehyde. Six species of *Oidium* behaved similarly. G. B.

The Culture of Yeast in Presence of Air with the Use of Carbamide as the Source of Nitrogen, and with different sources of Carbon. The Quotient of Sugar Assimilation. TH. BOKORNY (*Biochem. Zeitsch.*, 1917, **83**, 133—164).—A detailed account is given of a large number of experiments in which the increase in dry weight is determined when yeast is grown in diluted urine to which various sugars, glycerol, etc., are added as the source of carbon. The quotient of the sugar assimilation, that is, absolute increase in dry matter/amount of sugar employed, was determined in many cases. S. B. S.

Hexose-diphosphoric Acid, its Composition and its Rôle in Alcoholic Fermentation; the Behaviour of the Sugars with Three Carbon Atoms towards Yeast. CARL NEUBERG, ADAM LEVITE, and ERWIN SCHWENK (*Biochem. Zeitsch.*, 1917, **83**, 244—268).—The authors confirm the results of Harden and Young

in ascribing to hexose-phosphoric acid the formula $C_6H_{10}O_4(PO_4H_2)_2$. Its rotation is $[\alpha]_D^{15} = +3{\cdot}55°$, and it yields lævulose on hydrolysis. Neither it nor its salts can be fermented by living yeasts, even in presence of co-ferments or artificial activators, and this is not due to any toxic action on yeast cells. The esterification of phosphates takes place to the extent of only about 8% in presence of living cells even when toluene has been added, whereas the esterification of the phosphate by sugars is almost quantitative in presence of dried yeast or cell-free yeast juices. For these reasons, the formation of hexose-phosphate is regarded as a pathological process. There is no evidence, therefore, that a hexose-phosphate forms an intermediate stage in the degradation of a six-carbon into a three-carbon sugar. Neither glyceraldehyde nor dihydroxyacetone, furthermore, undergoes fermentation in the presence of yeast as does dextrose or lævulose, even in presence of activators, and this is shown not to be due to any toxic action on the yeast. Furthermore, trioses on distillation yield methylglyoxal, which can be separated in the form of its *p*-nitrophenylosazone, and this reaction is quantitative. On subjecting hexose-phosphoric acid prepared in different ways to this process, no triose could be detected. All evidence, therefore, is against the theories that the trioses are intermediary products of sugar fermentation and that hexose-phosphoric acids play a part in the production of such products (theory of Lebedev and others). S. B. S.

Pharmacological Studies of the Ipecacuanha Alkaloids and some Synthetic Derivatives of Cephaeline. III. Protozoöcidal and Bactericidal Action. A. L. WALTERS, W. F. BAKER, and E. W. KOCH (*J. Pharm. Expt. Ther.*, 1917, **10**, 341—364. Compare Walters, Eckler, and Koch, A., 1917, i, 717).—When solutions of emetine hydrochloride of 0·0005% strength are in contact with cultures of amœbas for an hour, many of the amœbas are destroyed, but transplants from these cultures to fresh agar plates show a certain amount of growth of amœbas which is retarded or delayed, due probably to the development of encysted or resistant forms. Stronger solutions of emetine hydrochloride are more toxic, but even when a 1% solution is employed, some amœbas may still be living at the end of an hour. The propyl and *iso*amyl ethers of cephaeline are more toxic towards amœbas than emetine.

Methylating cephaeline to form emetine is known to increase the toxic action towards *Endamœba buccalis* and paramœcia, and the substitution of the methyl group by ethyl, propyl, butyl, *iso*amyl, or allyl further intensifies this action. Cephaeline *iso*amyl ether phosphate is the most effective alkaloid of this group in killing paramœcia, being fifteen to twenty times as potent as emetine phosphate.

Tested on *Staphylococcus aureus* in the manner described, cephaeline propyl ether phosphate is bactericidal in solutions of 0·5% strength, and the corresponding *iso*amyl ether in solutions of

0·025% strength. Both these derivatives are much stronger than emetine in bactericidal action. H. W. B.

The Disinfectant Action of Quinine Derivatives on Diphtheria Bacilli. HANS SCHAEFFER (*Biochem. Zeitsch.*, 1917, **83**, 269—314).—Quinine shows an inhibitory action towards diphtheria bacilli in a concentration of 1 : 10,000. This action is not greater in the cases of hydrocupreine and its methyl, ethyl, and *iso*propyl derivatives. *iso*Butylcupreine is, however, more active, being antiseptic in a concentration of 1 : 50,000. *iso*Amyl, hexyl, heptyl, and octyl derivatives show increased antiseptic activity with increasing molecular weight, the octyl derivative being active in the concentration 1 : 750,000. The decyl derivative is less active (1 : 500,000), and from this substance onwards the activity of the derivatives progressively diminishes with increasing molecular weight until the cetyl derivative is active only in a concentration of 1 : 5000. The lethal action of the disinfectants runs for the most part parallel with their inhibitory action; an exception was found in the case of hexylhydrocupreine, which has a greater antiseptic action than its next lower homologue (*iso*amylhydrocupreine), but a smaller disinfecting action. The monhydrochlorides of the alkaloid were more active than the dihydrochlorides. The hydrocupreine derivatives showed good disinfecting action in human serum. S. B. S.

Behaviour of some Organic Substances in Plants. IX. G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1917, **47**, ii, 109—130. Compare A., 1917, i, 681).—The experiments described in the first part of this paper were carried out by watering germinating seeds or plants with dilute solutions (0·1%) of various organic substances. Mandelonitrile almost prevents germination, but when it is administered to seedlings, their growth is not prevented, although the mature plants have a habit of growth so abnormal as to give the appearance of a new species. In such plants hydrogen cyanide and benzaldehyde could not be detected either before or after the addition of emulsin. Normal adult plants are killed if mandelonitrile is administered to them.

Amygdalin does not prevent germination. Strychnine does not prevent germination, but has poisonous effects afterwards. Nicotine hinders germination and affects growing plants adversely. Morphine and caffeine resemble strychnine in their action.

In the second part of the paper experiments are described dealing with the action of triturated spinach on solutions of various organic substances, toluene being added to prevent putrefaction, and a slow current of oxygen being passed to assist any oxidative processes. The escaping gas is passed through barium hydroxide solution and the precipitated barium carbonate is weighed. In these conditions, catechol and saligenin are acted on to a considerable extent, tartaric acid and salicylic acid to a lesser extent, whilst benzoic acid, pyridine, piperidine, and nicotine remain unaltered.

Permeability. V. The Swelling of Plant Tissue in Water and its Relation to Temperature and Various Dissolved Substances. WALTER STILES and INGVAR JØRGENSEN (*Ann. Bot.*, 1917, **31**, 415—434).—Experiments with uniform disks of potatoes and carrots show that these vegetables, when immersed in distilled water, absorb water (swell) for some days before equilibrium is attained, and then it is maintained for several days. The rate of swelling of carrot is much greater than that of potato, the amount of swelling being influenced by the previous history of the tissue. In tap water the swelling is less than in distilled water, and equilibrium is not maintained for so long, a shrinkage of the tissue ultimately occurring. Rise of temperature causes an increase in the rate of swelling. In solutions of sodium chloride or sucrose, the swelling of potato or carrot diminishes with increase in the concentration of the solution, and may become a shrinkage. For the potato the approximate concentrations of isotonic solutions are $N/8$-sodium chloride and $M/4$-sucrose, and for the carrot $N/3$-sodium chloride. With the primary alcohols, preliminary swelling takes place in solutions of much higher concentration than isotonic solutions, and is followed by shrinkage in all concentrations. This shrinkage is due to toxic action and not to plasmolysis. Acids behave in a manner similar to the primary alcohols. W. G.

Tuba, an East Indian Poison for Fish. T. ISHIKAWA (*Tokyo Igakkwai Zasshi*, 1916, **30**, 45—46; *Jap. Med. Lit.*, 1917, **1**, 7—8; from *Chem. Abstr.*, 1917, **11**, 2371).—Tuba is the Malay name for the plant *Derris elliptica*, Benth., and is used to kill fish. *Tubatoxin*, $C_{18}H_{18}O_5$, forms white crystals from alcohol, m. p. 163·5°, soluble in most organic solvents, but not in water or in acids and alkalis; it reduces ammoniacal silver and alkaline copper solutions; a sensitive colour test is described. Tubatoxin produces in fish, frogs, and mammals general motor paralysis. The lethal dose for a rabbit (intravenous) is 0·0009 gram per kilo. Compare also Greshoff, A., 1891, 335; van Sillevoldt, A., 1900, i, 109; Power, A., 1903, ii, 323. G. B.

Chemical Constituents of Uzara Root. W. HENNIG (*Arch. Pharm.*, 1917, **255**, 382—405).—Uzara root, the valuable anti-diarrhœtic properties of which have been described by Gürber (*Münch. med. Woch.*, 1911, No. 40), appears to be identical with Warsicky's ithongua (*Ber. deut. Pharm. Ges.*, 1916, **26**, 266).

The dried, alcoholic extract of the root, which is known as uzaron, has been examined, and only one of the three crystalline substances mentioned by Gürber (*loc. cit.*) has been obtained. Uzaron is shaken with hot water (4 parts); the clear, aqueous solution, when cold, is separated from the upper layer of fatty and resinous substances, treated with freshly prepared 20% tannin solution so long as a precipitate is obtained (an excess is to be avoided), the mixture is stirred for twenty-four hours, the brown, plastic mass which has separated is collected, kneaded in a current of water, made into

a viscous broth with zinc oxide and water, and evaporated to dryness. The residual mass is finely powdered, extracted with methyl alcohol in a Haussmann vacuum distillation apparatus, the excess of alcohol is distilled from the extract, and the residue, which after being dried over sulphuric acid in a desiccator represents about 50% of the uzaron, is shaken for many hours with cold water; the insoluble portion is finally purified by repeated crystallisation from 50% alcohol and from hot water. The product is a glucoside, uzarin, the yield being about 10% of the uzaron or about 2·5% of the uzara root. *Uzarin*, $C_{75}H_{108}O_{30},9H_2O$, slender, colourless needles, m. p. about 210°, decomp. about 200°, is sparingly soluble in aqueous sodium hydroxide and in the usual solvents at the ordinary temperature, but dissolves comparatively easily in hot water. The solution has a neutral reaction, gives a precipitate with tannic acid, but not with neutral or basic lead acetate, and exerts a slight reducing action on bismuth nitrate, Fehling's soluiton, and ammoniacal silver nitrate after prolonged boiling. The colour reactions of uzarin are described. The glucoside does not contain methoxyl groups. It is easily hydrolysed by hot 2% sulphuric acid, yielding 1 mol. of propyl alcohol (identified in the form of barium propionate) and 3 mols. each of dextrose and uzaridin, a portion of the latter being obtained as anhydrouzaridin (see below). *Uzaridin*, $C_{18}H_{24}O_5$, forms colourless leaflets containing $\frac{1}{2}H_2O$, and when anhydrous has decomp. about 246°. It is insoluble in water, but dissolves in hot dilute alcohol, the solution having an intensely bitter taste. The *triacetyl* derivative, prepared by boiling with acetic anhydride, forms large, colourless needles, m. p. 225—227°, and when it is hydrolysed by boiling alcoholic $N/2$-potassium hydroxide, the amount of alkali neutralised is more than that corresponding with three acetyl groups. Under the same treatment, uzaridin itself is found to neutralise potassium hydroxide, although in what way cannot at present be stated.

Anhydrouzaridin, $C_{18}H_{22}O_4$, forms colourless needles containing $\frac{1}{2}H_2O$, and when anhydrous has decomp. 208—214°.

The alcoholic mother liquors obtained during the purification of urazin contain a small amount of a second glucoside, which is amorphous and differs from uzarin in its physiological action and in its extremely bitter taste. C. S.

Toxicity of Galactose and Mannose for Green Plants and the Antagonistic Action of other Sugars towards these. L. Knudsen (*Amer. J. Bot.*, 1917, **4**, 430—437; from *Physiol. Abstr.*, 1917, **2**, 561).—Plants were grown in culture tubes on agar with a modified Pfeffer's salt solution under conditions excluding micro-organisms. Galactose and mannose in 0·025 molar solutions were very toxic to the roots of peas and wheat. Dextrose and sucrose act as antidotes. G. B.

Organic Plant Poisons. I. Hydrocyanic Acid. Winifred E. Brenchley (*Ann. Bot.*, 1917, **31**, 447—456).—Hydrocyanic acid

is very toxic to peas and barley. Down to a dilution of 1 in 100,000, peas are killed either immediately or after a short interval of poor growth. In the case of barley, strong concentrations kill the plant, but at the above dilution there is a period during which no growth occurs, after which there is slight progress, but no normal growth. Sodium cyanide is just as toxic as hydrocyanic acid, but formic acid, except in very high concentrations, is comparatively harmless to barley. In no case was there any indication of stimulation in peas or barley, even at very great dilutions, with any of the compounds tested.

Pea plants killed by hydrocyanic acid shrivel from the cotyledons upwards, and the roots contract intensely. Barley roots will not enter strong solutions, but often put out laterals which stop short at the surface of the solution. W. G.

Effect of Sulphur on Different Crops and Soils. O. M. SHEDD (*J. Agric. Research*, 1917, **11**, 91—103).—Soja beans, clover, oats, lucerne, and wheat were grown in pots on eight different types of soil, which received applications of flowers of sulphur at the rates of 100 lb. and 200 lb. per acre, together with calcium carbonate and other fertilisers as applied to the controls. It was found that the sulphur increased the production of some crops, had no effect on others, and on some was injurious, the results depending on the crop and soil. On the whole, there was a majority of small increases. The sulphur increased the total sulphur and sulphate-sulphur of the crop. In the cases of clover and lucerne, the excess sulphur in the plants was in the form of sulphate, but in soja beans part of the excess was in another form, not necessarily protein, since an increased protein content was not always found with an increased sulphur content.

Germination tests with sixteen varieties of seeds showed that all except two formed a greater or less amount of sulphate on germinating, the increase varying from 0·0 to 0·035% on the weight of seed. W. G.

Nitrogen, Chlorine, and Sulphates in Rain and Snow. E. LYLE PECK (*Chem. News*, 1917, **116**, 283—284).—A continuation of the work of Artis (compare A., 1916, i, 304). Forty-one samples of rain and snow were examined between October, 1916, and June, 1917. The following results, expressed as parts per million, were obtained: sulphate, 4·3—36·39; nitrate, 0·10—0·50; nitrite, 0·0005—0·208; nitrogen in free ammonia, 0·097—0·872; nitrogen in albuminoid ammonia, 0·057—0·68; chlorine, 2·84—18·62. The chlorine was most constant, being 7·1 parts per million in twenty of the samples. The total fall during the period amounted to 15·86 in. of rain and 22 in. of snow. W. G.

Organic Chemistry.

A System of Organic Nomenclature. AUSTIN M. PATTERSON and CARLETON E. CURRAN (*J. Amer. Chem. Soc.*, 1917, **39**, 1623—1638).—An account, with examples, of the principles observed by the authors in their work of indexing organic compounds for the forthcoming Decennial Index of *Chemical Abstracts*.

J. C. W.

Solubility of Iodoform in Glycerol. CHIARIA (*Giorn. Farm. Chim.*, 1917, **66**, 94—96; from *Chem. Zentr.*, 1917, ii, 483).—The solubility of iodoform in glycerol (D^{15} 1·256) is 0·123%.

R. V. S.

The Cause of the Anomalies shown in the Dissociation of Amylene Hydrobromide and its Consequences. ALB. COLSON (*Compt. rend.*, 1918, **166**, 71—73).—The irregularities occurring in the dissociation of amylene hydrobromide, b. p. 107°, when heated for a long time at 184° under different pressures (compare Lemoine, A., 1891, 970), are shown to be due to the partial conversion of this hydrobromide, $CMe_2Br\cdot CH_2Me$, into its isomeride, $CHMe_2\cdot CHMeBr$, b. p. 124°. W. G.

An Alcohol Receipt of the Eighth Century. H. DEGERING (*Sitzungsber. K. Akad. Wiss. Berlin*, 1917, 503—515; from *Chem. Zentr.*, 1917, ii, 366—367).—A manuscript of the twelfth century lately received by the Royal Library in Berlin gives a recipe for the preparation of "*aqua ardens*" which agrees with another made known by Puccinotti from a manuscript at San Gimignano. Both texts are probably derived from an original belonging to the eighth century. The process described must have yielded at least 35 vol. %, for the sulphur test is described, and burning sulphur cannot be extinguished with a more watery liquid. R. V. S.

The Action of Phosphoryl Chloride on Methyl or Ethyl Alcohol. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **101**, 225—228. Compare A., 1917, i, 625).—Experiments have now been made to determine what by-products are formed during this reaction. If excess of ethyl alcohol is used, and the reaction mixture distilled at 215—220°, a small quantity of distillate (3—5% of the weight of the mixture) is obtained containing normal pyro- and ortho-esters. By neutralising the product from the action of excess of alcohol on phosphoryl chloride with barium hydroxide, using phenolphthalein as indicator, from 50—70% of the product is obtained as the salt, $BaC_2H_5PO_4$. It is shown experimentally that the tri-ester, Et_3PO_4, is decomposed at 100° by dry hydrogen chloride, with formation of the mono-ester, according to the equa-

plex being prepared from the sulphate of the alkaloid and then fractionally crystallised. The potassium and ammonium salts of the active complex could then be obtained by the action of potassium or ammonium iodide.

The asymmetry of the complex in question is not due to the asymmetry of the cobalt atom, but to a molecular asymmetry, which is different from Werner's types I and II; it is therefore called type III of molecular asymmetry.

Since the dinitrodiammino-oxalatocobalt compound is readily obtained from the tetranitrodiamminocobalt compound by the action of oxalic acid, it follows that the two ammonia groups in the latter compound are in the *cis*-position.

The least soluble fraction of the *brucine* salt,

$$[Co(NH_3)_2(NO_2)_2C_2O_4]H,C_{23}H_{26}O_4N_2,H_2O,$$

crystallised in brown needles, aggregating in radial form, and had $[\alpha]_D^{27.5}$ $-70.7°$; its solution in water was not stable, the free alkaloid gradually being deposited. The most soluble fraction gave crystals having $[\alpha]_D^{28}+68.3°$. The *potassium* salts,

$$[Co(NH_3)_2(NO_2)_2C_2O_4]K,1\tfrac{1}{2}H_2O,$$

obtained from the respective brucine salts, gave $[\alpha]_D^{27} \pm 115°$.

The least soluble *strychnine* salt,

$$[Co(NH_3)_2(NO_2)_2C_2O_4]H,C_{21}H_{22}O_2N_2,H_2O,$$

gave a potassium salt having $[\alpha]_D^{27}-104°$, but the strychnine salt could not be prepared pure, owing to its instability. The *dextro*-potassium salt could not be obtained from the strychnine salt.

With cinchonine, the least soluble fraction separated as pale brown needles, having the formula

$$[Co(NH_3)_2(NO_2)_2C_2O_4]H,C_{19}H_{22}ON_2,$$

and $[\alpha]_D^{27}$ $+149°$; the potassium salt derived from it had $[\alpha]_D^{27}+111°$. The more soluble fraction could not be isolated.

Ammonium salts were similarly obtained, having $[\alpha]_D^{27}-107°$ and $+116°$ respectively. T. S. P.

Method of Producing Acetaldehyde. E. F. SCHELLER (U.S. Pats., 1244901 and 1244902, 1917; from *J. Soc. Chem. Ind.*, 1918, 20A).—Purified acetylene mixed with steam is passed over a heated catalyst consisting of oxides or combinations of oxides; the exhausted or poisoned catalyst, for example, molybdic acid, may be regenerated by heating in a current of gas containing oxygen, for example, air. D. F. T.

The Method of Oxidation and the Oxidation Products of *l*-Arabinose and *l*-Xylose in Alkaline Solutions with Air and with Cupric Hydroxide. J. U. NEF, OSCAR F. HEDENBURG, and J. W. E. GLATTFELD (*J. Amer. Chem. Soc.*, 1917, **39**, 1638—1652. Compare A., 1914, i, 490).—An account, with full experimental details, of the identification of the products formed by the oxidation of *l*-arabinose and *l*-xylose in alkaline solutions.

Formic acid, calcium glycollate, *l*-erythrono-γ-lactone, *d*-threonophenylhydrazide, quinine *l*-glycerate, and calcium *d*-glycerate were actually obtained from *l*-arabinose after oxidation with air, and

glycollic acid, oxalic acid, and *l*-arabono-γ-lactone after oxidation with cupric hydroxide. *l*-Xylose gave formic acid, *l*-threonophenylhydrazide, *d*-erythrono-γ-lactone, calcium glycollate, and calcium *l*-glycerate when oxidised by air, and *l*-xylono-γ-lactone, *d*-xylono-γ-lactone, glycollic acid, and oxalic acid when heated with alkaline cupric hydroxide. J. C. W.

The Auto-oxidation of Sugars. L. Berczeller and E. Szegö (*Biochem. Zeitsch.*, 1917, **84**, 1—36).—Sugar in alkaline solution was shaken in the presence of air, and the influence of various substances added to the solution on the rate of oxidation was ascertained. The oxidation was measured by determining the diminution of pressure in the reaction flask after varying intervals. Some substances, such as methylene-blue, promote oxidation. The influence of tartrate and other substances on the oxidation of sugar in alkaline copper solutions was investigated. Charcoal was found to promote oxidation. S. B. S.

Lactose. A. Smits and J. Gillis (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 520—532. Compare Hudson, A., 1908, i, 952; ii, 665).—The α-anhydrous form of lactose is metastable not only below 93°, but also up to its m. p., 222·8°. The hydrate when heated at 125° in the dry condition gives the α-anhydrous form, but in the presence of its saturated solution at the same temperature always gives the β-form. The authors consider that lactose hydrate is the hydrate of the α-form, and that consequently *its dehydration is accompanied by a transition of the α- into the β*-anhydrous form, the transformation temperature, 93·5°, being really a transformation-dehydration point. As a consequence of this, the system water–lactose must be considered as a pseudoternary system, for which the authors have derived the isotherm diagram. [See also *J. Soc. Chem. Ind.*, 1918, 133A.] W. G.

Influence of different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. II. H. I. Waterman (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 382—391. Compare A., 1917, i, 195, 631).—An extension of the study to the influence of α-aminobutyric acid, valine, leucine, asparagine, glutamic acid, and tyrosine. The results in every case agree with those obtained from the amino-acids previously studied.

Aniline and pyridine have no influence on the action of sodium hydroxide on dextrose, but they retard the inversion of sucrose by hydrochloric acid. [See also *J. Soc. Chem. Ind.*, 1918, 133A.] W. G.

Adsorption ... **I. The Starch-Iodine Compl**... ...*eitsch.*, 1917, **84**, 106—117).—It ... otassium iodide is not necessary f... . The imbibition temperature of ... out 1° above that

LIBRARY
TNAU, Coimbatore - 3
000000123

of pure starch. Starch takes up more iodine at a lower than at a higher temperature. A secondary adsorption of iodine by starch can be demonstrated. Adsorption equilibrium between starch and iodine takes place more rapidly in dilute than in concentrated solutions. S. B. S.

Action of Methylene Iodide on Des-dimethylPiperidine (ε-Dimethylamino-Δ^{a}-pentene). AMAND VALEUR and ÉMILE LUCE (*Compt. rend.*, 1918, **166**, 163—164).—Methylene iodide does not cause cyclisation when it acts on ε-dimethylamino-Δ^{a}-pentene, but the compound, $C_8H_{17}NI_2$, obtained (compare Ladenberg, A., 1882, 534) is shown to be *methylene-des-dimethylpiperidine iodide* [*dimethyliodomethyl-Δ^{4}-pentenylammonium iodide*],

$$CH_2{:}CH{\cdot}[CH_2]_3{\cdot}NMe_2I{\cdot}CH_2I,$$

m. p. 163°, which when boiled with hydriodic acid in the presence of phosphorus gives *dimethyliodomethyl-δ-iodopentylammonium iodide*, $CH_3{\cdot}CHI{\cdot}[CH_2]_3{\cdot}NMe_2I{\cdot}CH_2I$, m. p. 136·5—137·5°. This compound with moist silver oxide gives a quaternary ammonium hydroxide which on treatment with potassium iodide yields a *compound*, $C_8H_{17}NI_2$, m. p. 143—144°, isomeric with the one described above. W. G.

The Free Affinity of the Copper Salts of the Imino-acids. J. V. DUBSKY and M. SPRITZMANN (*J. pr. Chem.*, 1917, [ii], **96**, 112—122).—The copper salt of iminodiacetic acid (Heintz, *Annalen*, 1862, **124**, 297; 1870, **156**, 51) in aqueous ammonia gives a deep blue solution which on evaporation deposits violet-blue needles of an additive compound of the composition $C_4H_8O_4N_2Cu,3H_2O$; in view of the composition of the corresponding compound derived from nitrosoiminodiacetic acid (see below), the constitution is probably $NH\left<\begin{matrix}CH_2{\cdot}CO_2\\CH_2{\cdot}CO_2\end{matrix}\right>Cu\ldots.NH_3$. In a similar manner, the bluish-green, microcrystalline *copper* salt, $C_4H_4O_5N_2Cu,2\frac{1}{2}H_2O$, of nitrosoiminodiacetic acid yields a violet-blue ammonia *additive* compound of the probable constitution $NO{\cdot}N\left<\begin{matrix}CH_2{\cdot}CO_2\\CH_2{\cdot}CO_2\end{matrix}\right>Cu\left<\begin{matrix}NH_3\\NH_3\end{matrix}\right.,2H_2O$, and the green *copper* salt of nitroiminodiacetic acid forms a violet-blue *additive* compound, to which is ascribed the formula $NO_2{\cdot}N\left<\begin{matrix}CH_2{\cdot}CO_2\\CH_2{\cdot}CO_2\end{matrix}\right>Cu\left<\begin{matrix}NH_3\\NH_3\end{matrix}\right.,H_2O$. The *copper* salt, $C_{10}H_9O_4NCu,H_2O$ (green needles), of phenyliminodiacetic acid, and the copper salts of iminodipropionic and nitroiminodipropionic acids with ammonia form respectively the *compounds* $C_{10}H_9O_4NCu,NH_3$ (bluish-green needles and prisms), $C_6H_{12}O_4N_2Cu,1\frac{1}{2}H_2O$ (pale blue crystals), and $C_6H_{14}O_6N_4Cu,2H_2O$ (violet-blue). In all these ammonia derivatives the copper atom is regarded as assuming a maximum valency of four. With the salts of nitrilotriacetic acid, $N(CH_2{\cdot}CO_2H)_3$, the behaviour was less regular; the bluish-green normal *copper* salt, $C_{12}H_{12}O_{12}N_2Cu_3,7H_2O$,

yielded pale blue crystals of a violet-blue ammonia compound, $C_{12}H_{27}O_{12}N_7Cu_3,4H_2O$, whereas the pale blue acid *copper* salt, $C_6H_7O_8NCu$, gave no definite product with ammonia. D. F. T.

Salt Formation with Nitroso-, Nitro-, and Phenyliminodiacetic Acids. J. V. DUBSKY and M. SPRITZMANN (*J. pr. Chem.*, 1917, [ii], **96**, 105—111).—Nitrosoiminodiacetic acid,

$$NO\cdot N(CH_2\cdot CO_2H)_2,$$

is conveniently prepared by the action of nitrous fumes on an aqueous suspension of iminodiacetic acid; the nitroso-acid is dibasic and forms an *ammonium* salt, a colourless, microcrystalline powder with $\frac{1}{2}H_2O$, and a colourless, crystalline *zinc* salt with $2H_2O$. Nitroiminodiacetic acid, $NO_2\cdot N(CH_2\cdot CO_2H)_2$ (Franchimont and Dubsky, A., 1916, i, 467), which is also dibasic, was converted through its *ammonium* salt, colourless leaflets with $1H_2O$, into the colourless *silver* salt, *barium* salt, crystalline mass with $2H_2O$, and *zinc* salt, an explosive, crystalline mass. Phenyliminodiacetic acid in aqueous solution reacts with silver nitrate, giving a *silver* salt, $C_{10}H_{10}O_4NAg$, needles, but the interaction of the diammonium salt with silver nitrate yields a *disilver* salt, $C_{10}H_9O_4NAg_2$, the precipitate, which is white at first, rapidly becoming yellow; the *zinc* salt, $C_{10}H_9O_4NZn,3H_2O$, was also prepared from the ammonium salt by double decomposition with zinc sulphate. With these acids, no double salts were observed of the type yielded by iminodiacetic and iminodipropionic acids.

D. F. T.

Constitution of Carbamides. V. Mechanism of the Decomposition of Urea when Heated in Solution with Alkalis and with Acids respectively. The Hydrolysis of Metallic Cyanates. EMIL ALPHONSE WERNER (T., 1918, **113**, 84—99. Compare T., 1913, **103**, 1013).—If a solution of urea in aqueous barium hydroxide is heated, ammonia can be detected in the vapour as soon as the boiling point is reached, but some minutes elapse before any barium carbonate appears. It follows, therefore, that the equation $CH_4ON_2 + Ba(OH)_2 = BaCO_3 + 2NH_3$ does not represent the facts, and that urea is not hydrolysed in this sense. The decomposition of urea by hydrolytic agents is more correctly represented in two stages: first, the dissociation of urea, which is the ammonium salt of ketonic cyanic acid, into ammonia and cyanic acid, and, secondly, the hydrolysis of the cyanic acid or alkali cyanate. Under comparable conditions, the rate at which urea is decomposed is greater in the presence of sodium hydroxide than in the presence of hydrochloric acid, because the proportion of free urea is greater in alkaline solutions than in acid, and only free urea suffers decomposition. Thus, in *N*-solutions, 55% of urea hydrochloride is dissociated into its components,

$$NH{:}C(OH)\cdot NH_2,HCl \longrightarrow NH{:}C{<}^{NH_3}_{O} + HCl;$$

whilst the acidic property of urea is so slight that a salt of the

formula $NH{:}C(ONa){\cdot}NH_2$ would only exist in solutions containing much urea and much alkali.

The dissociation of urea into ammonia and cyanic acid does not take place in sterile solutions, either acid or alkaline, to any appreciable extent below 90°. Thus, the velocity of the decomposition of urea at 98·2°, 71·25°, and 61·05° respectively is as 83·6 : 2·77 : 0·715. This can be verified by testing the solution from time to time with silver nitrate or barium hydroxide. The enzyme, urease, which brings about speedy decomposition at ordinary temperatures, apparently promotes direct hydrolysis of undissociated urea, for it has no influence on potassium cyanate.

The well-known fact that alcohol retards the decomposition of urea in solution, but accelerates the transformation of ammonium cyanate into urea, can only be explained satisfactorily in the light of these dissociation theories. In the first case, alcohol really retards the hydrolysis of the cyanic acid formed by dissociation of the urea, and in the second it promotes the dissociation of ammonium cyanate into ammonia and enolic cyanic acid, but does not interfere with the tautomerisation of the acid and its reunion in the ketonic form with ammonia to give urea.

The formation of urea from other cyanates than ammonium cyanate can be explained in a similar manner. Thus, the hydrolysis of potassium cyanate at ordinary temperatures is indicated by the equations: (1) $KOCN + H_2O \rightleftharpoons KOH + (HO{\cdot}CN \rightleftharpoons HN{:}CO)$, (2) $HO{\cdot}CN + H_2O = NH_3 + CO_2$, (3) $CO_2 + KOH = KHCO_3$, (4) $HN{:}CO + NH_3 = HN{:}C{<}^{NH_3}_{O}$, and $HO{\cdot}CN + NH_3 = NH_4O{\cdot}CN$. At higher temperatures than 80°, no ammonium cyanate would be formed.

For experimental details, see the original. J. C. W.

Preparation of Cyanamide. A. E. Osterberg and E. C. Kendall (*J. Biol. Chem.*, 1917, **32**, 297—298).—Calcium cyanamide is mixed with water, and carbon dioxide passed in until a neutral or only slightly alkaline reaction is reached. The temperature must be maintained below 40°. In these circumstances, the calcium cyanamide is quantitatively decomposed; and, after filtering off the precipitated calcium carbonate, the cyanamide is recovered from the filtrate by concentrating in a vacuum and subsequently extracting with ether. In this way, 55 grams of pure crystallised cyanamide are obtained from 200 grams of the calcium salt, corresponding with a yield of 92% of the theoretical. [Compare *J. Soc. Chem. Ind.*, 1918, **37**, 107A.] H. W. B.

Cyanuric Acid as an Oxidation Product of Uric Acid. Its probable Identity with Tetracarbimide. C. S. Venable and F. J. Moore (*J. Amer. Chem. Soc.*, 1917, **39**, 1750—1755).—Under the conditions described by Scholtz (A., 1902, i, 140), uric acid may be oxidised to cyanuric acid. With slight modifications, the yield of this product may be nearly 50% of the theoretical amount. The cyanuric acid prepared by this method has been

thoroughly identified, and it is more than likely that Scholtz was wrong in regarding his product as tetracarbimide. J. C. W.

New Preparation of Aliphatic Nitriles by Catalysis. ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 121—123).—Aluminium oxide can be used as a catalyst in place of thorium oxide for the preparation of nitriles from the esters of cyclic acids by the action of ammonia (compare this vol., i, 68), only in this case the gas evolved consists of ethylene and hydrogen in the proportion of 2:1 if ethyl esters are used. The reaction may be applied to aliphatic esters with equal success, but in this case, with thorium oxide, a certain amount of aldehyde-ammonia is produced, and with aluminium oxide some amide corresponding with the nitrile. [See also *J. Soc. Chem. Ind.*, 1918, 137A.] W. G.

New Method of Formation of Nitriles by Catalysis. ALPH. MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 215—217. Compare preceding abstract).—When the mixed vapours of an aldehyde and ammonia are passed over thorium oxide at 420—440°, the products are the corresponding nitrile, water, and some products of condensation of the aldehyde and ammonia. The method has been applied with success both to aliphatic and aromatic nitriles. [See also *J. Soc. Chem. Ind.*, 1918, 137A.] W. G.

A New Method of Dehydration of Oximes by Catalysis. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1918, [iv], **23**, 18—20).—Aldoximes were dehydrated by passing their vapour over aluminium oxide or thorium oxide heated at 340—360°, the corresponding nitrile being obtained. Dehydration also occurred under similar conditions with two ketoximes, *iso*butyronoxime and *iso*valeronoxime, the products in these cases being nitriles less rich in carbon. W. G.

The Action of Trioxymethylene on the Various Hydrocarbons in the Presence of Aluminium Chloride. G. B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1918, **40**, 329).—A question of priority between Nastjukov and the author. [See A., 1915, i, 227, 953.] L. A. C

Extraction of Pure Dimethylnaphthalenes from Coal Tar Oils. GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P., 301079, 1916; from *Chem. Zentr.*, 1917, ii, 713—714).—The neutral purified fraction of the oil, b. p. 260—265°, or the solid hydrocarbon mixture obtainable from this is sulphonated by sulphuric acid, and the resulting sulphonic acids are reconverted into the corresponding parent hydrocarbons.

1:6-Dimethylnaphthalene obtained in this way is a colourless oil of faint characteristic odour, b. p. 265° (*picrate*, needles, m. p. 114°); the sulphonic acid forms a *sulphonamide*, needles, m. p. 185°, on fusion with potassium hydroxide yields a dimethyl-

naphthol, m. p. 82°, *and on reduction with sodium amalgam undergoes scission of the sulphonyl group. Oxidation with dilute nitric acid converts the hydrocarbon into a carboxylic and a dicarboxylic acid, the latter being identical with 1:6-naphthalenedicarboxylic* acid prepared from 1:6-naphthylaminesulphonic acid, whilst the former when heated with hydrochloric acid loses carbon dioxide with formation of 2-methylnaphthalene. Chromic acid oxidises the dimethylnaphthalene to dimethyl-α-naphthaquinone, m. p. 95°, which is further oxidisable by potassium permanganate to *o*-methylphthalic acid.

2:6-Dimethylnaphthalene, leaflets, m. p. 109—110°, b. p. 260—261°, is oxidised by chromic acid to 2:6-*dimethyl-α-naphthaquinone*, m. p. 136—137°, and is convertible through the sulphonic acid into a dimethyl-β-naphthol, m. p. 172°.

2:7-Dimethylnaphthalene, leaflets, m. p. 96—97°, b. p. 262°, forms a solid sulphonic acid (*sodium* salt, needles), and on oxidation with chromic acid yields a *dimethyl-α-naphthaquinone*, m. p. 114—115°, which is further oxidisable by permanganate to trimellitic acid. D. F. T.

Separation of Secondary Amines produced in the Catalytic Hydrogenation of Aniline. G. Fouque (*Compt. rend.*, 1917, **165**, 1062—1065).—Catalytic hydrogenation of aniline yields *cyclo*hexylamine, di*cyclo*hexylamine, *cyclo*hexylaniline, and diphenylamine, together with smaller quantities of benzene, *cyclo*hexane, and tar. For the separation of the secondary amines, a method has been based on the following facts. (*a*) Di*cyclo*hexylamine hydrate forms a solid carbonate and three non-hydrolysable sulphates; (*b*) *cyclo*hexylaniline does not form a carbonate, but yields a normal sulphate, a sesquisulphate, and a hydrogen sulphate, which are hydrolysable, but dissolve in water acidified with sulphuric acid; (*c*) aniline does not form a carbonate; (*d*) diphenylamine sulphate has not been isolated. By repeated fractional distillation under ordinary and reduced pressure, the products are separated into fractions, one of which contains only aniline and di*cyclo*hexylamine, and another consists of a mixture of di*cyclo*hexylamine, *cyclo*hexylaniline, and diphenylamine. Each fraction, after the addition of water and ether, is saturated for several hours with carbon dioxide, and the aqueous solution of di*cyclo*hexylamine carbonate is separated, filtered, and neutralised with sulphuric acid. On evaporating the liquid, octahedral crystals of the normal *sulphate* of di*cyclo*hexylamine separate, whilst the *hydrogen sulphate* separates on treating the mother liquors with excess of sulphuric acid. The amine is obtained by dissolving the successive deposits of crystals in water and distilling the solution with sodium hydroxide under reduced pressure. It is a colourless, oily liquid boiling at 135° (under pressure of 20 mm.). The residue from which the di*cyclo*hexylamine carbonate was separated may consist of an ethereal solution of aniline or of a mixture of *cyclo*hexylaniline and diphenylamine with ether. After evaporation of the ether, it is heated with dilute sulphuric

acid, cooled, and filtered, the process being continued so long as the filtrate gives an orange coloration with a mixture of dilute sulphuric and nitric acids. Evaporation of the united filtrates yields deposits of crystals of *cyclo*hexylaniline sesquisulphate, whilst a little di*cyclo*hexylamine hydrogen sulphate may be obtained from the mother liquor. *cyclo*Hexylaniline may be separated from its sesquisulphate by means of warm dilute ammonia solution, and decanting and distilling the oily layer under reduced pressure. It is a strongly refractive liquid, boiling at 157°/20 mm. The solid residue of impure diphenylamine is purified by distillation and crystallisation from ether. C. A. M.

Intermediate Products (Formomethylanilide Derivatives) suitable for the Manufacture of Colouring Matters. H. LEVINSTEIN and G. T. MORGAN (Eng. Pat., 111321, 1916; from *J. Soc. Chem. Ind.*, 1918, 5A).—Formomethylanilide, also its halogen or alkyloxy-derivatives and homologues with a free para-position to the amino-group, may be nitrated at −5° to +20° with formation of the corresponding *p*-nitroformomethylanilide compounds; p-*nitroformomethylanilide* forms pale yellow prisms or needles, m. p. 119—120°. These products on reduction with iron borings and dilute formic or acetic acid at 85—100° are converted into the corresponding *p*-amino-compounds; the unsubstituted p-*aminoformomethylanilide*, $HCO\cdot NMe\cdot C_6H_4\cdot NH_2$, forms almost colourless needles, m. p. 115—116°. D. F. T.

Reduction of Phenylethylamine. ALBERT WEINHAGEN (*Biochem. J.*, 1917, **11**, 272—276).—Phenylethylamine prepared from phenylalanine differs from the synthetic product in that the latter resists reduction by the method of Willstätter and Hatt (A., 1912, i, 545), whilst the former is completely reduced to the hexahydro-compound (*cyclo*hexylethylamine). The synthetic product decolorises permanganate solution very slowly, whilst the other acts almost instantaneously. It is pointed out that Bernthsen remarked certain minor differences between synthetic phenylethylamine and that produced from phenylalanine. [See also *J. Soc. Chem. Ind.*, 1918, March.] J. H. L.

Bromo-alkylated Aromatic Amines. I. J. VON BRAUN, K. HEIDER, and E. MÜLLER (*Ber.*, 1917, **50**, 1637—1651).—When methylaniline is heated with ethylene dibromide at 100°, diphenyldiethylethylenediamine is not the only product. The first runnings of the basic distillate contain methyl-β-bromoethylaniline,

$$NMePh\cdot CH_2\cdot CH_2Br,$$

and the yield of this may be increased to 35% of the methylaniline employed if the proportion of bromide to base is 3 mols. to 2 mols. The new bromo-alkylated base is most remarkably reactive; it can be brominated, nitrated, etc., in the ring like any other tertiary aromatic amine; it has the reactions of tertiary amines in general, but, most important of all, it is capable of all the reactions of ethyl bromide.

Full details of the economical production of the base are given together with notes on the recovery of the unchanged ethylene dibromide and methylaniline, and the *tert.*-ethylenediamine *Methyl-β-bromoethylaniline* is a very pale yellow, somewhat heavy oil, b. p. 140—144°/13 mm., which becomes dark in the air without really suffering much change. The *picrate* has m. p. 125°, and the *methiodide*, m. p. 122°. It reacts with bases as follows methylaniline gives diphenyldimethylethylenediamine,

$$C_2H_4(NMePh)_2,$$

m. p. 51°; dimethylamine gives *phenyltrimethylethylenediamine* b. p. 144—146°/23 mm., which forms a *dipicrate*, yellow leaflets m. p. 171°; trimethylamine yields *β-phenylmethylaminoethyltrimethylammonium bromide*, $NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$, as a very hygroscopic, white mass, m. p. 165°. The base may also be brominated or nitrated, giving oily products, but *p-nitrosomethyl β-bromoethylaniline*, which is prepared exactly like *p*-nitrosodimethylaniline, is a stable, green mass, m. p. 70°. This reacts with trimethylamine to form a *p*-nitrosodialkylaniline derivative $NO{\cdot}C_6H_4{\cdot}NMe{\cdot}C_2H_4{\cdot}NMe_3Br$, which is soluble in water, the solution having the same green colour as the ethereal solution of *p*-nitrosodimethylaniline.

Under the influence of aluminium chloride, the base suffers condensation to 1-methyl-2:3-dihydroindole, the yield being about 35%. This is the first instance of the production of a dihydroindole by ring formation, and the method may prove to be of great service in the case of substituted dihydroindoles. By Fittig's method, the base may be converted into *diphenyldimethyltetramethylenediamine*, $C_4H_8(NMePh)_2$, m. p. 81°, b. p. 186—190°/5 mm. (*picrate*, m. p. 173°; *dimethiodide*, m. p. 180°), which give a brilliant greenish-blue coloration with oxidising agents (compare A., 1917, i, 175).

The base condenses with *p*-acetylaminophenol under the influence of sodium ethoxide to form *ω-phenylmethylaminophenacetin* $NHAc{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh$, in glistening leaflets, m. p. 102° and with morphine to give *ω-phenylmethylaminodionine*,

$$NMe{:}C_{16}H_{14}O(OH){\cdot}O{\cdot}C_2H_4{\cdot}NMePh,$$

as a yellow oil, which yields a *hydrochloride*, m. p. 110°. These are practically without the physiological action of unsubstituted phenacetin or dionine.

On boiling with aqueous-alcoholic potassium cyanide, the base yields *β-phenylmethylaminopropionitrile*, $NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, a pleasant-smelling oil, b. p. 186°/23 mm., together with a small quantity of the corresponding *amide*, m. p. 85°. This nitrile is interesting, compared with phenylmethylaminoacetonitrile* and other derivatives of aromatic amines containing the grouping $:N{\cdot}CH_2{\cdot}CN$, for the basic properties are not masked by the cyano group, and the *methiodide*, m. p. 132° (decomp.), is stable.

The base reacts with magnesium quite as readily as bromobenzene. When the magnesium compound is decomposed with ammonia and ammonium chloride, it yields methylethylaniline (65%) and diphenyldimethyltetramethylenediamine (35%), and

strange to say, these are the only products which can be obtained after treating the Grignard compound with ketones, although a vigorous reaction is observed to take place. Aldehydes react in a more normal manner, however, giving bases of the formula

$$NMePh\cdot CH_2\cdot CH_2\cdot CHR\cdot OH.$$

The separation of these from the mixture of products is a matter of considerable difficulty, requiring special methods from case to case. An account is given of the production of the compound $NMePh\cdot C_2H_4\cdot CHPr^{\alpha}\cdot OH$ from *n*-butaldehyde, and its isolation in the form of a *picrate*, long, red needles, m. p. 120°, and *platinichloride*, m. p. 214° (decomp.). The failure of the reaction with ketones recalls the fact that disubstituted amides, $R\cdot CO\cdot NR_2$, react vigorously with organomagnesium compounds, but are regenerated if the products are treated with dilute acids, whilst formamides, $H\cdot CO\cdot NR_2$, give aldehydes. It is suggested that the primary products are additive compounds with quadrivalent oxygen, thus, $R_2{:}C{:}O<^{MgX}_{R}$, and that in the case of the above base there are steric hindrances against rearrangement into compounds, $R_3C\cdot MgX$.

J. C. W.

Di-*n*-butylaniline. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, **113**, 99—111. Compare this vol., i, 10).—If *n*-butyl chloride is heated with aniline in an autoclave at 130—140°, a very high yield of mono-*n*-butylaniline is soon obtained, and if this is heated with more *n*-butyl chloride at 180° under pressure, a good yield of di-*n*-butylaniline is produced. This has been converted by normal methods into the following series of compounds: *A*, *p*-nitrosodi-*n*-butylaniline and *p*-phenylenedi-*n*-butyldiamine, $C_6H_5\cdot N(C_4H_9)_2 \longrightarrow NO\cdot C_6H_4\cdot N(C_4H_9)_2 \longrightarrow NH_2\cdot C_6H_4\cdot N(C_4H_9)_2$; *B*, 4-di-*n*-butylaminoazobenzene-4′-sulphonate, by means of diazotised sulphanilic acid, and this, by reduction, into the above diamine. Similarly, mono-*n*-butylaniline has been coupled with diazotised sulphanilic acid and the azo-compound reduced to *p*-phenylene-*n*-butyldiamine.

For some unaccountable reason, Karrer was unable to obtain the *p*-nitroso-compound or to couple the tertiary base with diazotised sulphanilic acid (A., 1915, i, 1073).

Typical salts and other derivatives of these compounds are also described, but the original should be consulted for the details.

J. C. W.

Phototropy and Thermotropy. VIII. Cinnamylideneamines. 2 : 4-Dihydroxybenzylideneamines. ALFRED SENIER and PATRICK HUGH GALLAGHER (T., 1918, **113**, 28—35. Compare A., 1915, i, 397, 877, and earlier).—Various amines have been condensed with cinnamaldehyde and 2 : 4-dihydroxybenzaldehyde in order to gather, if possible, new material for studies on phototropy and thermotropy. Of the many new Schiff's bases thus obtained, nearly all are found to exhibit thermotropic changes, but none are phototropic. Many of them, however,

change permanently into polymorphic forms on exposure to actinic light. Solutions in acetic acid or chloroform are usually deeper in colour than those in light petroleum, benzene, or acetone, and the 2:4-dihydroxybenzylidene compounds are green in dilute solutions and yellow in concentrated solutions.

For experimental details, see the original. J. C. W.

The Sulphonation of β-Naphthylamine. ARTHUR GEORGE GREEN and KAPILRAM H. VAKIL (T., 1918, **113**, 35—44).—It is well known that the 5-, 6-, 7-, and 8-sulphonic acids can be obtained by the direct sulphonation of β-naphthylamine, but it appeared to be of importance in the dye industry to learn something of the mechanism of the reactions, the circumstances favouring the production of the individual isomerides, and the conditions under which one may be converted into another. The present work, therefore, is a detailed study with those aims.

Within temperatures from 20° to 80°, the product contains 97—99·5% of the 5- and 8-acids. The ratio between these does not vary very much from about two parts of the 8-isomeride to three of the 5-acid, neither has time (one to ten hours) nor concentration of the acid (92% H_2SO_4 to an acid with 20% SO_3) much influence on this ratio, except that the lowest temperatures and shortest time are favourable to the production of the 5-acid. At temperatures below 80°, it follows that the sulphonation takes place simultaneously at positions 5 and 8. At higher temperatures and with longer periods of heating there is a falling off in the proportion of the 8-acid and an increased production of the 5-isomeride. This is explained by assuming that the 8-acid suffers hydrolysis to the *free* β-naphthylamine, which is then resulphonated, mainly to the 5-compound, as above. Simultaneously, the yield of the 6- and 7-isomerides increases also, reaching 7·5% with 96% sulphuric acid at 120° in five hours. It appears probable that disulphonic acids are produced, and that these suffer hydrolysis to monosulphonic acids, the 5-acid giving the 5:7- and then the 7-acid, and the 8-isomeride producing the 6:8- and then the 6-acid.

For details of the methods of separation and analysis, the original should be consulted. J. C. W.

Aspirin. V. Action of Salicylsalicylic Acid on the Solidification of Aspirin in Concentric Rings. D. E. TSAKALOTOS and S. HORSCH (*Bull. Soc. chim.*, 1918, [iv], **23**, 16—18).—Salicylsalicylic acid facilitates, but is not essential for, the formation of concentric rings during the crystallisation of aspirin from alcohol. W. G.

The Indene Series. V. J. VON BRAUN (*Ber.*, 1917, **50**, 1659—1661).—Hydrindone reacts with magnesium methyl iodide to form 1-hydroxy-1-methylhydrindene (A., 1913, i, 1364). This is reconverted into the original ketone by the action of alkalis, which is best demonstrated by leaving methyl-alcoholic solutions of the carbinol with anisaldehyde or *p*-dimethylamino-

benzaldehyde in contact with a few drops of sodium hydroxide, when the known condensation products of hydrindone and the aldehydes soon crystallise out.

1-*Hydroxy-1-ethylhydrindene*, $C_6H_4<\overset{CH_2}{\underset{CEt(OH)}{}}>CH_2$, a pleasant-smelling syrup, b. p. 123—125°/9 mm., D_4^{20} 1·063, behaves similarly. The tendency to part with the elements of water increases with increasing magnitude of the 1-alkyl group. The methyl compound may be distilled under atmospheric pressure, but the ethyl homologue changes thereby into 1-*ethylindene*, a mobile liquid, b. p. 226°, D_4^{22} 0·9732. With larger radicles, the indenes are already produced during the Grignard reaction, and may be purified by distillation under ordinary pressures. 1-n-*Butylindene*, a very pleasant-smelling liquid, b. p. 252—255°, 120°/10 mm., D_4^{20} 0·9552, and 1-*phenylindene*, $C_6H_4<\overset{CH_2}{\underset{CPh}{}}>CH$, a pale yellow syrup, b. p. 200—201°/29 mm., D_4^{17} 1·0829, may be obtained directly from hydrindone in this way. J. C. W.

Preparation of 1-Hydroxyanthranol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 301452, 1916; from *Chem. Zentr.*, 1917, ii, 715).—By reducing 1-hydroxyanthraquinone with zinc in acid solution, it is possible to obtain 1-hydroxyanthranol, which is of value as a remedy for psoriasis. D. F. T.

Triphenylmethyl. XXVIII. Tautomerism of Triarylcarbinols. M. GOMBERG and L. C. JOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1674—1688. Compare A., 1916, i, 639).—The condensation of diphenylmethylene dichloride with phenols is a convenient method for the preparation of *p*-hydroxytriarylcarbinols. It has already been shown that compounds of this class, even if they contain certain substituents in the ortho-position with respect to the phenolic group, exist in two desmotropic forms, benzenoid and quinonoid. From a preliminary survey, however, it appears that substituents in the meta-position in these carbinols (ortho to the central carbon atom) often hinder tautomerism to quinonoid forms.

Thus diphenylmethylene dichloride combines with *m*-cresol to form *diphenyl-5-hydroxy-o-tolylcarbinol*, $OH\cdot CPh_2\cdot C_6H_3Me\cdot OH$, which can only be obtained in the colourless, benzenoid form, m. p. 114°. This has also been synthesised as follows: *m*-cresol and carbon tetrachloride are converted by the Tiemann and Reimer method into 5-hydroxy-*o*-toluic acid, and the ethyl ester of this is treated with magnesium phenyl bromide. The carbinol combines with many solvents, in molecular proportions; *compounds* with acetic acid, alcohol, benzene, chloroform, and carbon tetrachloride are described. The 5-*methylcarbonato*-derivative,

$$OH\cdot CPh_2\cdot C_6H_3Me\cdot O\cdot CO_2Me,$$

from methyl chloroformate, has m. p. 118; the 5-*ethylcarbonato*-derivative has m. p. 128°; the 5-*benzoyloxy*-derivative has m. p. 103°; and the 5-*acetoxy*-compound has m. p. 136°. The carbinol loses water at about its m. p., forming *diphenyl-3-methylquino-*

methane, $CPh_2:C_6H_3Me:O$, in red needles, m. p. 183°. This fuchsone absorbs two molecular proportions of hydrogen chloride, one of which is removed by evacuation.

The carbinol is also transformed into the fuchsone hydrochloride when treated with hydrogen chloride, so the triarylmethyl chloride required for the preparation of the free radicle cannot be obtained. The above ethylcarbonato-derivative, however, can be converted into *diphenyl-5-ethylcarbonato-o-tolylcarbinyl chloride*,

$$CO_2Et\cdot O\cdot C_6H_3Me\cdot CPh_2Cl,$$

m. p. 96—97°, from which the chlorine can be removed by means of finely divided silver, as usual. The authors have not been able to isolate the free radicle as a solid, but have obtained its *peroxide*, R_2O_2, m. p. 141—142°, by exposing the deep cherry-red, benzene solution to the air until almost bleached and then evaporating.

If the original carbinol is brominated in acetic acid solution, it yields *diphenyl-4:6-dibromo-5-hydroxy-o-tolylcarbinol*; this exists as an almost colourless benzenoid modification, m. p. 146·5—147·5°, and in the yellowish-red, quinonoid form, m. p. 147—148°. The latter loses water more rapidly than the former on heating, but both ultimately change at 150° into the dark red *diphenyl-2:6-dibromo-3-methylquinomethane*, $CPh_2:C_6HMeBr_2:O$. The corresponding colourless and yellow *diphenyl-4:6-dichloro-5-hydroxy-o-tolylcarbinols* have m. p. 135—137°.

m-*Methoxyphenol* also reacts with diphenylmethylene dichloride, giving *4-hydroxy-2-methoxytriphenylcarbinol*, of which only a colourless form, m. p. 132° (decomp.) has been obtained. This crystallises with demi-molecular proportions of benzene and carbon tetrachloride. Its constitution is established by proving that it is not the other possible product, namely, *2-hydroxy-4-methoxytriphenylcarbinol*, which has m. p. 154°, decomp. 158°. This has been synthesised as follows: resorcylic acid is converted by methylation into 2-hydroxy-4-methoxybenzoic acid, and the ethyl ester of this is treated with magnesium phenyl bromide. J. C. W.

The State of Saturation of Chromophores. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1623—1625. Compare A., 1917, i, 391).—A reply to Lifschitz (A., 1917, i, 558). J. C. W.

Production of Aminoalkyl Esters and Alkylaminoalkyl Esters of *p*-Aminobenzoic Acid. W. BAKER and LEVINSTEIN, LTD. (Eng. Pat., 111328, 1916; from *J. Soc. Chem. Ind.*, 1918, 4—5A).—Alkyl esters of *p*-aminobenzoic acid are heated at 150—180° with an amino- or alkylamino-alcohol in the presence of the aluminium compound of the amino-alcohol, when the simple alcohol is displaced from the ester and distils off; the excess of amino-alcohol may then be removed by distillation in a vacuum. Instead of adding the aluminium derivative of the amino-alcohol as such, it can be formed in the mixture by the addition of aluminium amalgam. *Diethylaminoethyl p-aminobenzoate* prepared in this way forms a colourless *hydrochloride*. D. F. T.

Process for Producing Carbamides and Thiocarbamides of the Aromatic (Benzene or Carbazole) Series. FARBENFABRIKEN VORM. F. BAYER & Co. (Eng. Pat., 8591, 1916; from *J. Soc. Chem. Ind.*, 1918, 20A). Carbamide or thiocarbamide compounds can be obtained by the action of carbonyl chloride or thiocarbonyl chloride on aminoacylaminosulphonic acids of the benzene or carbazole series. m-*Nitrobenzoyl*-m-*aminobenzoylaminosulphosalicylic acid*,

$NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_2(OH)(SO_3H) \cdot CO_2H$,

obtained by the action of *m*-nitrobenzoyl chloride on *m*-aminobenzoylaminosulphosalicylic acid, on reduction yields m-*aminobenzoyl*-m-*aminobenzoylaminosulphosalicylic acid*,

$NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_2(OH)(SO_3H) \cdot CO_2H$,

and this, like bis[*m*-aminobenzoyl]-aminocarbazoledisulphonic acid, can by means of the named reagents be converted into carbamide derivatives possessing valuable therapeutic properties. D. F. T.

The Fluorescence of Cyano-compounds. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1614—1623).—The remarkable fluorescence exhibited by the platinocyanides would lead to the supposition that the cyanogen radicle has a favourable influence on this phenomenon, and makes a study of organic cyanogen compounds particularly interesting. Quite simple nitriles are found to be fluorescent; benzonitrile, for example, is strongly reactive in the ultra-violet. 2:5-Dimethoxybenzonitrile might therefore be expected to be very fluorescent, as it combines the properties of very fluorescent *p*-dimethoxybenzene with those of the cyano-group. As a matter of fact, the eye can scarcely detect any fluorescence (compare Grignard, Bellet, and Courtot, A., 1916, i, 487), but in the ultra-violet *N*/1000-alcoholic solutions are most strongly fluorescent. *o*-Aminobenzonitrile should also be very active, but no mention of the property has been made in the literature. Alcoholic solutions exhibit a powerful violet fluorescence, which is displaced towards the ultra-violet in indifferent solvents. Among more complicated nitriles, a number of striking examples have recently been described (A., 1917, i, 394).

It is remarkable that many organic cyanogen compounds are only fluorescent in the solid state, like barium platinocyanide. The compound $NMe_2 \cdot C_6H_4 \cdot CH{:}CPh \cdot CN$ (*ibid.*) is an example of this. The corresponding free amino-compound, $NH_2 \cdot C_6H_4 \cdot CH{:}CPh \cdot CN$, is also only fluorescent in the solid state, but the isomeride,

$NH_2 \cdot C_6H_4 \cdot C(CN){:}CHPh$,

is strongly active both in the solid form and in solution. The intimate connexion between fluorescence and constitution is here exemplified in a new way.

The last-named compound is a representative of a new class of substances which are strongly fluorescent in solution, namely, compounds containing the group $-CH{:}C(CN) \cdot C_6H_4 \cdot NH_2$, of which examples are now given.

Nitro-groups are generally a hindrance to fluorescence, but the

cyano-group can often overcome this influence. Thus, the compounds $OMe\cdot C_6H_4\cdot CH:C(CN)\cdot C_6H_4\cdot NO_2$ and

$$C_6H_4[CH:C(CN)\cdot C_6H_4\cdot NO_2]_2$$

are fluorescent, at any rate in the solid state, whilst the analogous substances free from the cyano-group are very feebly active.

Red compounds, as a rule, are likewise seldom fluorescent, but even red nitriles are known which are brilliantly fluorescent. When viewed in the light of a mercury lamp behind a blue screen so arranged that substances like lead chromate or cinnabar appear to be black, the red compound, $NMe_2\cdot C_6H_4\cdot CH:C(CN)\cdot SO_2Ph$ (Tröger and Bremer, A., 1910, i, 113), shines with a vermillion light; the red nitrile, $NMe_2\cdot C_6H_4\cdot CH:CBz\cdot CN$ (*loc. cit.*), appears to be brick-red; *p*-dimethylaminobenzylidenemalonitrile is orange-red, and the compound, $NMe_2\cdot C_6H_4\cdot N:CPh\cdot CN$ (Ehrlich and Sachs, A., 1899, i, 883), appears to be bright brick-red.

[With AD. JEUTTER.]—*a-p-Aminophenylcinnamonitrile* (p-*amino-a-cyanostilbene*), yellow crystals, m. p. 122°, blue fluorescence in benzene, ether, or chloroform, green in alcohol, bluish-violet in carbon tetrachloride or light petroleum, is obtained by reduction of the nitro-compound, which is prepared by the condensation of *p*-nitrobenzyl cyanide with benzaldehyde.

a-p-Aminophenyl-γ-benzylideneacrylonitrile (*a-cyano-a-aminophenyl-δ-phenylbutadiene*), which forms pale brown crystals, m. p. 153°, is obtained by reduction of the product of the condensation of cinnamaldehyde with *p-nitrobenzyl cyanide. The fluorescence* exhibited is as follows: solid, feebly red behind the blue screen; solution in pyridine or acetone, bright green; in glacial acetic acid, ether, or chloroform, greenish-blue; in alcohol, yellowish-green; in light petroleum, violet-blue; even in such au unfavourable solvent as carbon disulphide, a blue fluorescence is still manifest.

Dinitro-a:a'-dicyanodistyryl-4:4'-benzene,

$$C_6H_4[CH:C(CN)\cdot C_6H_4\cdot NO_2]_2,$$

yellow crystals, m. p. above 300°, is formed by condensing *p*-nitrobenzyl cyanide with terephthalaldehyde.

[With (FRL.) LILLY LUTZ.]—p-*Amino-a-phenylcinnamonitrile* (p-*amino-ω-cyanostilbene*), from the nitro-compound, forms yellow crystals, m. p. 143°. *a-p-Aminophenyl-2-methoxycinnamonitrile*, stout, yellow needles, m. p. 105°, is obtained from the *nitro*-compound, $OMe\cdot C_6H_4\cdot CH:C(CN)\cdot C_6H_4\cdot NO_2$ (lemon-yellow needles, m. p. 190°, brilliant lemon-yellow fluorescence behind the blue screen), which is prepared by the action of *p*-nitrobenzyl cyanide on *o*-methoxybenzaldehyde. *a-p-Aminophenyl-4-methoxycinnamonitrile* forms yellow needles, m. p. 151°, and its fluorescence is as follows: solid, moderate greenish-yellow; solutions in pyridine and alcohol, green, in acetone, blue, and in ether, violet-blue. *a-p-Aminophenyl-3:4-methylenedioxycinnamonitrile,*

$$CH_2:O_2:C_6H_3\cdot CH:C(CN)\cdot C_6H_4\cdot NH_2,$$

yellow needles; m. p. 174° (intense bluish-green fluorescence in pyridine), is obtained from the corresponding *nitro*-compound, yellow needles, m. p. 188° (strong orange-yellow fluorescence),

which is prepared by the condensation of *p*-nitrobenzyl cyanide and piperonaldehyde. J. C. W.

Mandeliminohydrin. JOHN EDWIN MACKENZIE (T., 1918, **113**, 1—3).—*Following Eschweiler's method for the preparation of* "iminohydrins" of *a*-hydroxy-acids (A., 1897, i, 399), the author has converted benzaldehydecyanohydrin into the iminoalkyl ether hydrochloride, OH·CHPh·C(OEt):NH,HCl, and this by means of silver hydroxide into "*mandeliminohydrin*," m. p. 173—179° (decomp.) (see following abstract). J. C. W.

Amidine Salts, and the Constitution of the so-called Iminohydrins. HAROLD GORDON RULE (T., 1918, **113**, 3—20).—The iminohydrins or *iso*amides, which are usually prepared by the action of moist silver oxide on imino-ether hydrochlorides, or water on the free imino-ethers, were formulated by Eschweiler as OH·CR:NH (A., 1897, i, 399) and by Hantzsch as

NH:CR·O·NH_2:CR·OH

(A., 1901, i, 676). Hantzsch showed that the compounds are comparatively strong electrolytes, with molecular weights twice as great as Eschweiler supposed. "Glycolliminohydrin" hydrochloride and the sodium salt of "glycolliminohydrin" are, moreover, known to be considerably hydrolysed in aqueous solutions, and Walker, under whose inspiration the present paper and Mackenzie's note (preceding abstract) have been presented, finds that the degree of hydrolysis for *N*/8-solutions is about 50%. On the theory of amphoteric electrolytes, therefore, free "iminohydrins" should be very feeble conductors, but their conductivities are really as high as that of a salt, which is in conflict with Hantzsch's formula.

Hantzsch and Walker were both impressed with the fact that all "iminohydrins" described so far have been those of *a*-hydroxy-acids. The hydroxyl group is not a critical part of the molecule, however, for the methoxyacetic and phenylacetic derivatives have now been obtained, and the discovery has been made that the compounds are really amidine salts of the formula

NH_2·CR:NH,R·CO_2H.

Thus, "glycolliminohydrin" is glycollamidine glycollate, and "mandeliminohydrin" is mandelamidine mandelate,

OH·CHPh·C(NH_2):NH,CO_2H·CHPh·OH.

These two salts have been synthesised by the interaction of the amidine hydrochlorides and sodium glycollate or mandelate, as the case may be.

The hydrolysis of the imino-ethers by water is formulated thus: (1) OEt·CR:NH + $2H_2O$ = R·CO_2NH_4 + EtOH; (2) R·CO_2NH_4 + OEt·CR:NH = NH_2·CR:NH,R·CO_2H + EtOH. In this connexion, it is interesting to note that imino-ethers react with ammonium chloride, but not ammonia, to form amidine hydrochlorides (Knorr, A., 1917, i, 255).

In examining amidine salts of the hydroxy-acids, a number of Eschweiler's statements have been revised.

For experimental details, see the original. J. C. W.

Influence of the Replacement of a β-Hydrogen Atom by a Phenyl Group in α-Hydroxy-γ-phenylcrotonic and γ-Hydroxy-γ-phenylcrotonic Acids. J. BOUGAULT (*Bull. Soc. chim.*, 1918, [iv], **23**, 20—24).—The introduction of a β-phenyl-group into these acids considerably modifies the molecule, in that it prevents the reactions which are apparently the most characteristic of the groupings $\cdot CH{:}CH\cdot CH(OH)\cdot CO_2H$ and

$$\cdot CH(OH)\cdot CH{:}CH\cdot CO_2H.$$

Thus the reactions with alkalis, mineral acids, oxalic acid, iodine in excess, and sodium carbonate are all modified. W. G.

Nitration of 5- and 6-Acetylamino-3 : 4-dimethoxybenzoic Acids and 4-Acetylaminoveratrole. JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1918, **113**, 22—28).—The authors have recently been associated with Gibson in a study of the nitration of 2-acetylamino-3 : 4-dimethoxybenzoic acid and 3-acetylaminoveratrole (A., 1917, i, 203), and the present work is a natural sequel.

5-Acetylamino-3 : 4-dimethoxybenzoic acid, prepared from 5-nitrovanillin, yields the 6-nitro-compound, which may be converted into the known 6-nitroveratric acid, and also some 4 : 5-dinitro-3-acetylaminoveratrole (*ibid.*). In the case of 6-acetylamino-3 : 4-dimethoxybenzoic acid, the carboxyl group is displaced on nitration, the sole product being 5-nitro-4-acetylaminoveratrole, which may also be prepared by nitrating 4-acetylaminoveratrole, and can be converted into 4-nitroveratrole.

For experimental details, see the original. J. C. W.

Camphoceanaldehydic Acid (*tert.-sec.*) (**Camphoric Acid Semialdehyde**). **II.** J. BREDT (*J. pr. Chem.*, 1917, [ii], **96**, 65—72. See also A., 1917, i, 560).—Campholaldehydic acid is unstable both in its active and inactive modifications; not only does it readily undergo atmospheric oxidation, but also, when kept out of contact with air, the crystalline acid gradually becomes liquid, the alteration apparently being one of polymerisation. The aldehydic acid is therefore conveniently kept in the form of its acetyl derivative, viz., acetoxy-β-campholide, from which it is easily reobtained by hydrolysis with aqueous sodium carbonate.

[With L. ACKERMANN and J. DORREN.]—If *d*-camphoraldehydic acid is heated for eight hours at 100° in a sealed tube with acetic anhydride, the normal *l*-acetoxy-β-campholide, m. p. 126—128°, is obtained, together with an *isomeride*, prisms or tablets, m. p. 81—83°, $[\alpha]_D^{18}$ +95·77° in benzene; both products on hydrolysis with sodium carbonate yield the original aldehydic acid. In a similar manner, *dl*-camphoraldehydic acid on prolonged heating with acetic anhydride gives rise to a mixture of the *dl*-acetoxy-campholide, m. p. 97—98°, already described (*loc. cit.*), together with an *isomeride*, tablets, m. p. 73—74°. The active and inactive compounds already known, together with their isomerides now

described, do not reduce potassium permanganate in neutral aqueous solution, and therefore are all free from the aldehydic group; the isomerism is therefore regarded as similar to that of the *endo*- and *exo*-borneols, and due to the position of the acetoxy-group with respect to the plane of the six-atom ring.

The failure of Rupe and Splittgerber (A., 1907, i, 1016) to obtain β-campholide by the action of nitrous acid on β-aminocampholic acid is ascribed to the conversion of the four-atom ring into a five-atom ring during the reaction, according to which view the liquid product of this reaction is to be regarded as the lactone of hydroxy-trimethyl*cyclo*hexanecarboxylic acid; such enlargements of the four-atom ring have already been observed (Demjanoff and Luschnikoff, A., 1903, i, 403; Errera, A., 1893, i, 108; 1894, i, 202).

In order to avoid the inconveniently high temperature (erroneously quoted as 600° instead of 400° in the earlier paper) necessary for the production of sodamide, a mixture of sodamide and potassamide is prepared by passing ammonia on to a mixture of the metals (2:1 by weight) at 270—280°. D. F. T.

Preparation of α-Naphtholphthalein. EMIL ALPHONSE WERNER (T., 1918, **113**, 20—21).—A mixture of α-naphthol, phthalic anhydride, and a small quantity of sulphuric acid is carefully heated at 60—65°. The yield is about 33% of the weight of α-naphthol, but is seriously diminished if the temperature rises above 65°.

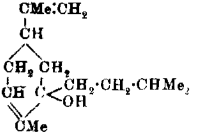
J. C. W.

Production of Anils of Hydroaromatic Ketones. GUSTAV REDDELIEN (D.R.-P., 301121, 1915; from *Chem. Zentr.*, 1917, ii, 714).—Anils are easily obtained by heating the hydroaromatic ketones with amino-compounds at 160—180° in the presence of a small quantity of a strong acid, for example, hydrochloric acid, as catalyst; instead of the acid, the corresponding salt of the amino-compound may be used, or, if the reaction is vigorous, even a metallic salt, for example, the zinc salt of the acid may be applied. Camphor when heated with aniline and aniline hydrochloride yields *camphoranil*, colourless needles, m. p. 13·5°, b. p. 164—165°/15 mm.; menthone and aniline react in the presence of the additive compound of zinc chloride and aniline, giving *menthoneanil*, a pale yellow oil, b. p. 162—172°/16 mm., whilst with *p*-anisidine, *menthone*-p-*anisil*, m. p. 61—62°, is formed; *carvoneanil*, obtained similarly, is a yellow oil, b. p. 179—181°/15 mm., which forms an exceptionally sensitive reagent for nitric acid, giving a deep blue coloration with this substance. D. F. T.

Decomposition of Oximinocamphor when Heated. E. SERNAGIOTTI (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 221—223). —Beckmann and Köster (A., 1893, i, 474) showed that, on fusion, α-benziloxime is converted into benzoic acid and benzonitrile, the hydroxyl of the :C:N·OH group passing to the adjacent carbonyl group. On the other hand, Kötz and Wunstorf (A., 1913, i, 1361) found that at 240° oximinocamphor is decomposed in a different manner, the products formed being dimethylheptenonitrile and

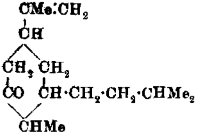
camphoric anhydride, although the grouping undergoing change is the same as in the previous case, namely, :C·CO·C(:NOH)·C:. The authors find, however, that at 206—207° oximinocamphor is rapidly decomposed with formation of the α-nitrile of camphoric acid, together with a green oil of ketonic or aldehydic character; the nitrile results from a reaction similar to that occurring with α-benziloxime. T. H. P.

Constituents of Ethereal Oils. Synthetical Experiments in the Unicyclic Sesquiterpene Series. F. W. SEMMLER, K. G. JONAS, and K. OELSNER (*Ber.*, 1917, **50**, 1838—1842).—The product of the action of magnesium *iso*amyl iodide on carvone contains not only *iso*amyl-α-dehydrophellandrene (following abstract), but small quantities of oxygenated compounds with higher b. p.'s.



One of these is the normal carbinol, tert-*isoamylcarveol* (annexed formula), which has b. p. 155—170°/12 mm., D^{20} 0·9217, n_D^{20} 1·4917, α_D^{20} −4°, and is the first synthetic unicyclic sesquiterpene alcohol. It loses water when treated with potassium hydrogen sulphate, and may be hydrogenated to form tert.-*isoamyltetrahydrocarveol*, b. p. 154—160°/17 mm., D^{20} 0·8908, n_D^{20} 1·4632, α_D^{20} −1·5°.

The other compound, which is formed in larger quantity if ether is used instead of benzene as the solvent, is the first synthetic sesquiterpene ketone. The *iso*amyl group is introduced at the double linking in the carvone ring instead of at the carbonyl group.

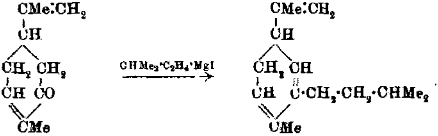


iso*Amyldihydrocarvone* (annexed formula) has b. p. 144—148°/10 mm., D^{20} 0·9022, n_D^{20} 1·47694, α_D^{20} −8°, forms an *oxime*, m. p. 135°, and may be reduced by sodium and alcohol to sec-*isoamyldihydrocarveol*. This has b. p. 150—155°/10 mm., D^{20} 0·8993, n_D^{20} 1·47449, α_D^{20} +1°, forms an *acetate*, b. p. 155—160°/11 mm., D^{20} 0·9227, n_D^{20} 1·46711, α_D^{20} +5°, and may be hydrogenated to sec.-*isoamyltetrahydrocarveol*, b. p. 145—152°/12 mm., D^{20} 0·8906, n_D^{20} 1·46855, α_D^{20} +1°. [See also *J. Soc. Chem. Ind.*, 1918, 137A.] J. C. W.

Constituents of Ethereal Oils. Gum Ammoniac Oil, and Synthetical Experiments on the Nature of its Constituents. F. W. SEMMLER, K. G. JONAS, and PAUL ROENISCH (*Ber.*, 1917, **50**, 1823—1837).—I. *Investigation of Gum Ammoniac Oil.*—The gum-resin, which is obtained in the first instance as a milky juice, from the umbelliferous plant *Dorema ammoniacum* and several *Ferula* species, yields about 0·3% of an oil on distillation. A sample of this, with D^{20} 0·8855, n_D^{20} 1·47233, and α_D^{20} +1·7°, has been submitted to a thorough investigation along the usual lines. The first fractions, b. p. 60—130°/10 mm., 19% of the oil, contain linalyl

10 mm., 20% of the oil, consists chiefly of a unicyclic, dihydrosesquiterpene, $C_{15}H_{26}$, to which the name *ferulene* is given; this has not been obtained pure, as the sample contains about 25% of a bicyclic sesquiterpene, $C_{15}H_{24}$, the constants, b. p. 124—126°/7 mm., D^{20} 0·8698, n_D^{20} 1·48423, α_D^{20} +6°, being in agreement with such a mixture; on reduction it yielded *tetrahydroferulene*, b. p. 118—120°/10 mm., D^{20} 0·8400, n_D^{20} 1·45810, α_D^{20} +4·2°. About 22% of the oil was found to have b. p. 145—155°/12 mm., D^{20} 0·8765, n_D^{20} 1·47160, α_D^{20} +3·5°, and to consist of an ethylenic, sesquiterpene ketone, to which the name *doremone* is assigned. This is the first record of a ketone of this class, either among natural or synthetic compounds. Doremone, $C_{15}H_{26}O$, forms an *oxime*, m. p. 88°, b. p. 160—165°/10 mm., D^{20} 0·8995, n_D^{20} 1·47914, α_D^{20} +2° (*acetate*, b. p. 180—195°/9 mm., D^{20} 0·9283, n_D^{20} 1·47370, α_D^{20} +1°), and a *semicarbazone*, m. p. 124°. It may be reduced by means of platinum and hydrogen to *tetrahydrodoremone*, $C_{15}H_{30}O$, b. p. 142—144°/12 mm., D^{20} 0·8434, n_D^{20} 1·44803, α_D^{20} +1·4°, and by means of sodium and alcohol to the ethylenic alcohol, *doremol*, $C_{15}H_{28}O$, b. p. 145—150°/12 mm., D^{20} 0·8702, n_D^{20} 1·47130, α_D^{20} +3°, which may be further reduced by platinum and hydrogen to *tetrahydrodoremol*, $C_{15}H_{32}O$, b. p. 140—145°/12 mm., D^{20} 0·8403, n_D^{20} 1·44818, α_D^{20} +2·8°, a paraffin alcohol with abnormal carbon chain. *Doremyl acetate*, b. p. 155—165°/12 mm., D^{20} 0·8896, n_D^{20} 1·46596, α_D^{20} +4·8°, is also present in the higher fractions. The highest fraction, b. p. above 175°/12 mm., contains cetyl alcohol, which has not hitherto been found in plants.

II. *Experiments on the Synthesis and Characterisation of Unicyclic and Olefinic Compounds of the Sesquiterpene Series.*—When carvone is treated with magnesium *iso*amyl iodide in benzene, it yields a unicyclic sesquiterpene, the intermediate carbinol readily losing the elements of water, thus:



The hydrocarbon, *iso*amyl-α-*dehydrophellandrene*, has b. p. 130—132°/11 mm., D^{20} 0·8679, n_D^{20} 1·49478, α_D^{20} +18·5°, does not form a solid compound with hydrogen chloride or suffer condensation to a bicyclic compound, which shows the absence of conjugated double linkings in the side chain, but it combines with six atomic proportions of hydrogen to form *iso*amyl*menthane*, $C_{15}H_{30}$, b. p. 131—133°/14 mm., D^{22} 0·8250, n_D^{22} 1·45562, α_D^{19} −1·5°.

Farnesol may be hydrogenated in the presence of platinum to form inactive *hexahydrofarnesol*, $C_{15}H_{32}O$, b. p. 145—155°/15 mm., D^{22} 0·8387, n_D^{20} 1·44525, with which the above doremol is obviously closely connected. [See also *J. Soc. Chem. Ind.*, 1918, 137A.]

The Essential Oil of Sea-samphire from different parts of France. MARCEL DELÉPINE and GASTON DE BELSUNCE (*Bull. Soc. chim.*, 1918, [iv], **23**, 24—35. Compare A., 1909, i, 642; 1910, i, 401).—The results of the analyses of oil of samphire (*Crithmum maritinum*) obtained from plants grown in different parts of France show that they all contain the characteristic constituents, namely, 5 : 6-dimethoxy-3 : 4-methylenedioxy-1-allylbenzene, the methyl ether of thymol, and crithmene. In some cases *p*-cymene and *d*-pinene, and a paraffin, m. p. 63°, were also obtained. [See also *J. Soc. Chem. Ind.*, 1918, 137A.] W. G.

The Colloidal Nature of Colophony. II. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 148—154. Compare this vol., i, 25). —Further observations which are said to be of interest in reference to the colloidal nature of resin. [See, further, *J. Soc. Chem. Ind.*, 1918, 130A.] H. M. D.

Natural Resins [Überwallungsharze]. IX. MAX BAMBERGER and HERBERT VON KLIMBURG (*Monatsh.*, 1917, **38**, 457. See also Bamberger and Renezeder, A., 1903, i, 643; 1899, i, 929; 1898, i, 88).—The resin obtained from the stone pine (*Pinus cembra*) possesses an odour recalling vanillin, becomes reddened on exposure to light, and has m. p. about 70°, acid number 127, and iodine number 112, but the value for the last is as low as 78·4 if the resin is previously purified by dissolving in alcohol and pouring into water acidified with hydrochloric acid; the methoxyl content is lower than in other natural resins, amounting only to 13 parts per 1000. Boiling water extracts from the resin caffeic acid and also small quantities of ferulic acid and vanillin, whilst the residual molten resin on fusion with potassium hydroxide yields *p*-hydroxybenzoic acid, catechol, protocatechuic acid, acetic acid, and a trace of butyric acid. As with the resins investigated earlier, stone pine resin, after extraction with water, can be separated into an α-resin soluble in ether and a β-resin insoluble in the same solvent, the α-resin, which has a much lower methoxyl content than the β-resin, predominating. Attempts to produce a resinol analogous to pinoresinol or lariciresinol (Bamberger, A., 1894, i, 109) were unsuccessful.

Lariciresinol when heated with zinc dust in a stream of hydrogen yields a distillate containing toluene, xylene, naphthalene, methylnaphthalene, a trace of guaiacol, and probably also cumene. Lariciresinol also gives a resinous ozonide, but the only decomposition product identified after shaking with water was hydrogen peroxide.

Pinoresinol is already known to contain two hydroxyl groups; by heating with alcohol and a little sulphuric acid, it can be converted into an amorphous *anhydro*-compound, $C_{19}H_{18}O_5$, which resists the action of methyl sulphate in alkaline solution, but on treatment with acetyl chloride yield diacetylpinoresinol.

D. F. T.

The Aloins. II. E. LÉGER (*Ann. Chim.*, 1917, [ix], **8**, 265—302. Compare A., 1917, i, 276).—A résumé of work already published

(compare A., 1912, i, 708; 1914, i, 309, 707; 1915, i, 889; 1916, i, 413). W. G.

Synthesis in the Pyran Series. J. VON BRAUN and Z. KÖHLER (*Ber.*, 1917, **50**, 1657—1658).—$\beta\beta'$-Di-iodoethyl ether has already been used in the synthesis of compounds containing the morpholine ring (I) (compare Clarke, T., 1912, **101**, 1788). It may also be applied to the preparation of pyran derivatives of the type (II).

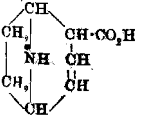
$$O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>N\cdot \qquad O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<$$

(I.) (II.)

Thus, ethyl disodiomalonate and $\beta\beta'$-di-iodoethyl ether react to form *ethyl tetrahydropyran-4:4-dicarboxylate*, b. p. 152—155°/21 mm. The free *acid* crystallises in colourless leaflets, m. p. 172—173°, and yields *tetrahydropyran-4-carboxylic acid*, m. p. 87°, when heated above its m. p. J. C. W.

Action of Hydrobromic Acid on Cinchonine and its Isomerides: Cinchoniline, Cinchonigine, and *apo*Cinchonine. E. LÉGER (*Compt. rend.*, 1918, **166**, 76—79. Compare Cordier von Löwenhaupt, A., 1899, i, 176).—When cinchonine or its isomerides are heated on a water-bath with hydrobromic acid (D 1·49), *there is addition of hydrogen bromide, but at the same* time isomerisation occurs. Thus, in the case of cinchonine, the mother liquors, after the separation of hydrobromocinchonine, contain cinchonigine, δ-cinchonine, *apo*cinchonine, cinchoniline in small amount, and an amorphous base, which the author names *cinchoniretine*, which is isomeric with cinchonine. From cinchonigine and *apo*cinchonine no cinchoniline was obtained. Further, although the four isomeric bases give the same hydrobromocinchonine, with cinchonigine and *apo*cinchonine there is a simultaneous formation of *hydrobromo*apo*cinchonine*. W. G.

Preparation of Derivatives of Alkaloids of the Cocaine Group. CHEMISCHE WERKE GRENZACH (D.R.-P., 301139, 1915; from *Chem. Zentr.*, 1917, ii, 714—715).—The compounds derived from alkaloids of the cocaine group by demethylation at the nitrogen atom, for example, anhydronorecgonine (tropene-2-carboxylic acid, annexed formula) and anhydrodihydronorecgonine (tropane-2-carboxylic acid) and their esters, on alkylation at the nitrogen atom by means of halogen-alkyl benzoates, yield compounds of marked pharmacological activity, showing similar properties to cocaine; they possess great local anæsthetic power, and are also sterilisable and less poisonous than cocaine. The ethyl ester of anhydroecgonine on treatment with cyanogen bromide and subsequent hydrolysis is convertible into anhydronorecgonine, of which the



ethyl ester, b. p. 146—151°/20 mm., reacts with γ-bromopropyl benzoate, with formation of oily *benzoxypropylanhydronorecgonine*

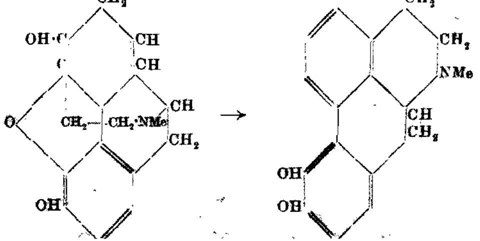
ethyl ester; hydrochloride, crystals, m. p. 116—117°. γ-Bromopropyl *p*-nitrobenzoate, m. p. 42°, b. p. 229—233°/17 mm., reacts with the ethyl ester of anhydronorecgonine, yielding *p-nitrobenzoxypropylanhydronorecgonine ethyl ester*, $C_{20}H_{24}O_6N_2$; *hydrochloride*, hygroscopic crystals, m. p. 154°; *picrate* difficulty crystallisable. On reduction with tin and hydrochloric acid, the nitro-compound is converted into *p-aminobenzoxypropylanhydronorecgonine ethyl ester*, $C_{20}H_{26}O_4N_2$; *hydrochloride*, hygroscopic and of no definite m. p.; *platinichloride*, m. p. 297°; *aurichloride*, m. p. 93°. ε-Bromoamyl benzoate and anhydronorecgonine ethyl ester react with formation of *benzoxyamylanhydronorecgonine ethyl ester* (*hydrochloride*, oily). Anhydrodihydronorecgonine ethyl ester, b. p. 135—138°, obtained by the reduction of anhydronorecgonine ethyl ester with hydrogen in the presence of a catalyst, reacts with γ-bromopropyl benzoate, giving *benzoxypropylanhydrodihydronorecgonine ethyl ester*, $C_{20}H_{27}O_4N$; *hydrochloride*, m. p. 142°; *platinichloride*, m. p. 94—95°; *aurichloride*, m. p. 127—128°.

D. F. T.

The Rotatory Power and Molecular Weight of Gitaline (ψ-Digitoxine). JAMES BURMANN (*Bull. Soc. chim.*, 1917, [iv], **21**, 290—293).—The author finds for gitaline carefully prepared and purified the values $[\alpha]_D^{15}$ −25·2° (in chloroform) and −18·8° (in alcohol), and for the molecular weight 539, by the ebullioscopic method, chloroform being the solvent. [See also *J. Soc. Chem. Ind.*, 1918, 136A.]

W. G.

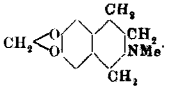
Constitution of the Morphine Alkaloids. Synthesis of *iso*Quinoline Derivatives. II. ADOLF KAUFMANN and NICLAUS DÜRST (*Ber.*, 1917, **50**, 1630—1637. Compare A., 1916, i, 502).—According to Knorr's researches on the morphine alkaloids, they are not *iso*quinoline derivatives, but yield such when heated with concentrated hydrochloric acid or zinc chloride solution, that is, by the rupture of the seven-membered nitrogen ring and closure of a new ring. This is illustrated by the change from morphine to *apo*morphine, thus:



After rupture of the "morphine" ring, and before closure to the *iso*quinoline nucleus, one of the three chains $\cdot NMe\cdot CH_2\cdot CH_2\cdot OH$, $\cdot NMe\cdot CH_2\cdot CH_2Cl$, or $\cdot NMe\cdot CH\colon CH_2$ might be present. In order to gain some idea as to the possibility of the first of these being formed, the authors have synthesised piperonyl-β-hydroxyethylmethylamine (I), and attempted to condense it to dihydrohydrastinine (II). Unlike the tertiary phenylethylamine (III), however, the *tert.*-benzylamine does not yield an *iso*quinoline.

$CH_2\colon O_2\colon C_6H_3\cdot CH_2\cdot NMe\cdot CH_2\cdot CH_2\cdot OH$ $\xrightarrow{\text{does not}}$
(I.)

$CH_2\colon O_2\colon C_6H_3\cdot CH_2\cdot CH_2\cdot NMe\cdot CH_2\cdot OH$ $\xrightarrow{\text{does}}$
(II.)


(III.)

This is probably due to the ease with which *tert.*-benzylamines decompose into benzyl alcohol and *sec.*-amines (Tiffeneau and Fuhrer, A., 1914, i, 517), for the present base is broken down on boiling with acetic anhydride into the compounds
$CH_2\colon O_2\colon C_6H_3\cdot CH_2\cdot OAc$
and $NMeAc\cdot C_2H_4\cdot OAc$.

Piperonaldehyde and methylamine are condensed to piperonylidenemethylamine, b. p. 128—129°/10·5 mm. (Andree, A., 1902, i, 210); this is reduced to piperonylmethylamine, b. p. 126·5°/10 mm., by means of hydrogen and spongy platinum, and this is condensed with ethylene oxide to 3:4-*methylenedioxybenzylmethyl-β-hydroxyethylamine* (I), b. p. 172—173°/10 mm. No agents have been found which can bring about the condensation of this base to dihydrohydrastinine (II). Hydrochloric acid at 100° converts it into the salt, $CH_2\colon O_2\colon C_6H_3\cdot CH_2\cdot NMe\cdot CH_2\cdot CH_2Cl,HCl$, and this also yields no dihydrohydrastinine, even when treated with zinc dust or aluminium chloride. On heating at 100°, the free chloro-base changes into *dipiperonylpiperazine dimethochloride*,

$$CH_2\colon O_2\colon C_6H_3\cdot CH_2\cdot \underset{Cl}{NMe}<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>\underset{Cl}{NMe}\cdot CH_2\cdot C_6H_3\colon O_2\colon CH_2,$$

m. p. 221° (decomp.) (*picrate*, m. p. 212°). [See also *J. Soc. Chem. Ind.*, 1918, 136A.] J. C. W.

Reactions of Piperidine with Organic Halogen Compounds in Ethereal Solutions. SARGENT G. POWELL and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1717—1723).—When reaction takes place between piperidine and organic haloids in dry ether, the primary products are additive compounds, being, in fact, the halogen hydracid salts of the *N*-derivatives of piperidine. These differ in stability towards water, heat, and bases, and decompose ultimately into the piperidine salt and substituted bases, thus: $C_5H_{10}NH + RX \rightarrow C_5H_{10}NR,HX \rightarrow C_5H_{10}NR + HX$; $C_5H_{10}NH + HX \rightarrow C_5H_{10}NH,HX$. The salts are obviously

obtained as precipitates, which are sometimes nearly pure additive products, sometimes nearly pure piperidine salts, but usually mixtures. The lower alkyl haloids react so quickly and in the dark that they give the purest additive compounds; iodides react more smoothly than bromides, and these more readily than chlorides. From the halogen estimation, the percentage of additive compound (*A.C.*) in the precipitate can be roughly estimated.

Methyl iodide gave pure 1-methylpiperidine hydriodide; *iso*propyl bromide gave piperidine hydrobromide; *iso*butyl iodide gave 1-iso*butylpiperidine hydriodide*, stout, prismatic needles, m. p. 131°; *iso*amyl chloride gave a precipitate containing 84% of *A.C.*; *iso*amyl bromide gave *A.C.* 0·8%; *iso*amyl iodide gave *A.C.* 61·5%; cetyl iodide gave *A.C.* 58·5%; benzyl chloride gave *A.C.* 66·8%; *epi*chlorohydrin gave *A.C.* 74·3%; ethyl chloroformate gave *A.C.* 8%. ββ-Dichloropropane yielded piperidine hydrochloride according to the equation $C_5H_{10}NH + CMe_2Cl_2 = C_5H_{10}NH,HCl + CH_2\!:\!CMeCl$; tetrachloroethane reacted according to the equation $B + C_2H_2Cl_4 = B,HCl + CHCl\!:\!CCl_2$; carbonyl chloride yielded the unstable compound, $CO(C_5H_{10}N)_2,2HCl$; acetyl thiocyanate gave nearly pure 1-*acetylpiperidine thiocyanate*, m. p. 83—85°; phenylpropionyl chloride, benzenesulphonyl chloride, arsenic trichloride, antimony trichloride, chromyl chloride, pentachloroethane, hexachloroethane, and carbon tetrachloride yielded only piperidine hydrochloride; *s*-dibromoethane gave piperidine hydrobromide; bromoform yielded *A.C.* 41%; acetyl bromide yielded *A.C.* 72%; and *iso*butyryl bromide gave *A.C.* 86·7%. J. C. W.

Nitroaminoquinolines. ADOLF KAUFMANN and OTTO ZELLER [with JULES MARTON] (*Ber.*, 1917, **50**, 1626—1630).—The *p*-toluenesulphonyl derivatives of aminoquinolines can very readily be nitrated, and the products are easily hydrolysed to the nitroamines by means of concentrated sulphuric acid.

5-Aminoquinoline, b. p. 184°/10 mm., m. p. 109—110°, forms a p-*toluenesulphonyl* compound, in stout, white needles, m. p. 203—204°, which reacts with nitric acid (D 1·5) at 60° to give 6:8-*dinitro*-5-p-*toluenesulphonylaminoquinoline*, m. p. 215°.

6-Aminoquinoline, b. p. 187°/11 mm., m. p. 118°, yields a p-*toluenesulphonyl* derivative, glistening, white crystals, m. p. 195°, which reacts with 60% nitric acid at 70° to form 5-*nitro*-6-p-*toluenesulphonylaminoquinoline*, glistening, yellow crystals, m. p. 168—169°, and this may be hydrolysed to 5-*nitro*-6-*aminoquinoline*, yellow needles, m. p. 178° (*picrate*, m. p. 270°). The position of the nitro-group follows from the fact that the product of the action of iron and hydrochloric acid, 5:6-*diaminoquinoline*, pale brown bundles of needles, m. p. 95°, reacts with phenanthraquinone to form a yellow *azine*, m. p. 287—288°.

8-Aminoquinoline, b. p. 157—162°/20—24 mm., m. p. 65°, yields a p-*toluenesulphonyl* compound, hard, white needles, m. p. 154—156°, which reacts with 60% nitric acid at 50° to form 5:7-*dinitro*-8-p-*toluenesulphonylaminoquinoline*, silky crystals, m. p. [illegible]—240° (decomp.), and a small amount of a more soluble mono-

nitro-derivative, m. p. 199—200°. These yield Claus's 5:7-dinitro-8-aminoquinoline, m. p. 187—188°, on hydrolysis.
J. C. W.

Phenazoxonium and its Simplest Derivatives. F. Kehrmann and A. Boubis (*Ber.*, 1917, **50**, 1662—1667. Compare A., 1914, i, 868; 1915, i, 586).—As an outcome of the discovery that phenazothionium forms both *meri-* and *holo*-quinonoid salts, it was suggested that a new investigation of the azoxoniums would prove that these are also normal in their behaviour towards acids. The present chemical and optical notices (following abstracts) show that the supposition was well founded.

The reddish-violet salts obtained by dissolving phenazoxine in sulphuric acid, whether dilute or concentrated, are *meri*-quinonoid, mono-acid salts. If hydrogen peroxide is added to the solutions in concentrated sulphuric or perchloric acid, yellow *holo*-quinonoid, di-acid salts are formed. These are unstable, but can be preserved for a short time at 0—10°. On diluting the yellow solutions with glacial acetic acid, the colour changes to wine-red, *holo*-quinonoid, mono-acid salts being formed. The *holo*-quinonoid, *monoperchlorate* (annexed formula), can even be isolated as an explosive, brown, glistening powder, but the successful preparation is a matter of chance, as the salt readily changes to the *meri*-quinonoid compound.

$$C_6H_4{\lessgtr}\genfrac{}{}{0pt}{}{N}{O}{>}C_6H_4 \quad \underset{ClO_4}{}$$

In the case of 3:9-dimethylphenazoxonium, dark red solutions of the *holo*-quinonoid di-acid sulphate may be obtained by dissolving the base in a mixture of the concentrated acid and hydrogen peroxide; on dilution with glacial acetic acid, orange-coloured solutions of the *holo*-quinonoid mono-acid salt result. A brownish-red, *holo*-quinonoid *picrate*, $C_{20}H_{14}O_8N_4$, and a dark violet, *meri*-quinonoid *monoperchlorate* may be isolated as crystalline powders.

5-Aminophenazoxonium yields an explosive, very dark green *holo*-quinonoid *perchlorate*, $NH_2{\cdot}C_{12}H_7N{:}O{\cdot}ClO_4$, which gives a blood-red solution of the *holo*-quinonoid di-acid salt in concentrated sulphuric acid. No tri-acid salt is formed.

3-Aminophenazoxonium perchlorate is a dark red, para-quinonoid salt, and not ortho-quinonoid, thus: $C_{12}H_7ON{:}NH_2{\cdot}ClO_4$. [See also *J. Soc. Chem. Ind.*, 1918, 119A.] J. C. W.

Quinoneimide Dyes. VII. Spectra of the Simplest Azoxine Dyes. F. Kehrmann and Maurice Sandoz (*Ber.*, 1917, **50**, 1667—1673).—An account, with tables and reproductions of the curves, of the absorption spectra of the salts of phenazoxonium, 3:9-dimethyl-, and 5- and 3-amino-phenazoxoniums (compare preceding abstract).

meri-Quinonoid phenazoxonium salts exhibit a band with maximum at λ 530 μμ; the *holo*-quinonoid, di-acid salts give a maximum at 460 μμ, and the mono-acid salts show two maxima, the principal one being at 530 μμ. For the dimethylphenazoxonium salts, the maxima are: *meri*-quinonoid, 570 μμ, and faint bands at 450 μμ

and in the extreme violet; *holo*-quinonoid, di-acid salts, 500 $\mu\mu$, and mono-acid salts, 560 $\mu\mu$.

The *holo*-quinonoid, mono-acid salts of 5-aminophenazoxonium give a maximum in the infra-red, whilst the di-acid salts have maxima at 535 $\mu\mu$ and 430 $\mu\mu$; the salts are therefore orthoquinonoid. The mono-acid salts of 3-aminophenazoxonium have maxima at 492 and 395 $\mu\mu$; the di-acid salts give maxima at 640 and 590 $\mu\mu$, which proves that these salts are para-quinonoid.

In the ultra-violet, all these salts give absorption bands with maxima at 265 and 285 $\mu\mu$. Phenazothionium salts, on the other hand, give one band, at 290 $\mu\mu$. [See also *J. Soc. Chem. Ind.*, 1918, 119A.] J. C. W.

Quinoneimide Dyes. VIII. Supplementary Observations on the Absorption Spectra of the Simplest Azothionium Compounds. F. KEHRMANN and M. SANDOZ (*Ber.*, 1917, **50**, 1673—1682. Compare A., 1915, i, 586).—The absorption spectra of the following phenazothionium salts are reproduced by curves and tables: *phenazothionium*: di-acid salts, yellowish-green, maxima in infra-red, at λ 520 $\mu\mu$ and 460 $\mu\mu$; mono-acid salts, blood-red, λ 518 and 435 $\mu\mu$; *6-methylphenazothionium*: di-acid salts, yellowish-green, λ 460 $\mu\mu$ and in infra-red; mono-acid salts, constitution in doubt, blood-red, λ 515 $\mu\mu$ and border of ultra-violet; *5-aminophenazothionium*: di-acid salts, yellowish-blood-red, λ 540 and 440 $\mu\mu$; mono-acid salts, yellowish-green, λ 410 $\mu\mu$ and infra-red.

[With A. BOUBIS.]—*5-Aminophenazothionium perchlorate* (annexed formula) may be obtained in moss-green, slender, explosive needles by oxidising 5-aminothiodiphenylamine with ferric chloride and perchloric acid. It gives solutions of the di-acid salt in concentrated sulphuric acid.

$$NH_2\cdot C_6H_3 <_{S}^{N}> C_6H_4 \quad (S\cdot ClO_4)$$

[With G. ROCHAT and A. BOUBIS.]—Thiodiphenylmethylamine is oxidised by means of sodium nitrite in glacial acetic acid to the sulphoxide, which gives a green solution of the di-acid salt of 6-methylphenazothionium in 70% perchloric acid. [See also *J. Soc. Chem. Ind.*, 1918, 119A.] J. C. W.

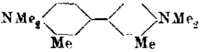
Quinoneimide Dyes. IX. Absorption Spectra of the Mono-acid Salts of Phenyl Derivatives of 3:9-Diaminophenazoxonium. F. KEHRMANN and M. SANDOZ (*Ber.*, 1917, **50**, 1682—1683).—The tables referred to in the preceding abstract also contain the following data: *3:9-diaminophenazoxonium monohydrochloride*, solutions in alcohol, bluish-violet, λ 593, 570, 545 $\mu\mu$; *3-amino-9-anilinophenazoxonium (9)-hydrochloride*, blue, λ 605 $\mu\mu$; *3:9-dianilinophenazoxonium monohydrochloride*, greenish-blue, λ 664 $\mu\mu$; *3:9-tetramethyldiaminophenazoxonium nitrite*, greenish-blue, λ 645, 588 $\mu\mu$; and *3-dimethylamino-9-anilinophenazoxonium (9)-monohydrochloride*, greenish-blue, λ 651 $\mu\mu$.

The fact is again emphasised that all the phenazothioniums

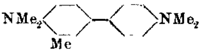
behave alike in the ultra-violet spectrum, exhibiting an absorption band at λ 290 $\mu\mu$, whilst the phenazoxoniums are all alike in giving two maxima, λ 265 and 285 $\mu\mu$. [See also *J. Soc. Chem. Ind.*, 1918, 119A.]

J. C. W.

Steric Hindrance. III. J. von Braun and M. Mintz (*Ber.*, 1917, **50**, 1651—1656. Compare A., 1913, i, 1333; 1916, i, 647). —In the first paper of this series, on tetramethyldiaminodiarylmethanes, it was shown that if both basic groups are encumbered by hindering neighbours, the compounds do not react at all readily with cyanogen bromide or iodoacetonitrile, but if only one group is sterically hindered, then reactions can take place at both tertiary amino-groups. Another example is now given; the compound (I) is inactive, but the base (II) reacts at both nitrogen atoms.



(I.)



(II.)

Tetramethyl-*o*-tolidine (I), prepared by heating *o*-tolidine with methyl iodide and sodium carbonate solution, reacts sluggishly with iodoacetonitrile to form *dimethyldicyanomethyl-o-tolidine*,

$$CN\cdot CH_2\cdot NMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot NMe\cdot CH_2\cdot CN,$$

m. p. 163°.

3-Methylbenzidine, from the reduction of *o*-methylazobenzene, forms a glassy mass, b. p. 225°/4 mm., and yields a *picrate*, m. p. 204°. If this is methylated by the above method, it gives the *methiodide*, $NMe_2\cdot C_6H_3Me\cdot C_6H_4\cdot NMe_3I$, m. p. 155—156°, which is converted by heating at 180—200°/4 mm. into *tetramethyl-3-methylbenzidine* (II), m. p. indefinite, 63—70°. This base forms a *picrate*, m. p. 193°, and a 6:6′-*dinitro*-compound, m. p. 110°, and reacts with cyanogen bromide to give *dicyanodimethyl-3-methylbenzidine*, $CN\cdot NMe\cdot C_6H_4\cdot C_6H_3Me\cdot NMe\cdot CN$, m. p. 138—139°, which may be hydrolysed to the oily *dimethyl-3-methylbenzidine*, this yielding a *dinitroso*-derivative, m. p. 195°. When the tertiary base (II) is warmed with iodoacetonitrile, three products are formed, one being insoluble in hot water, another insoluble in cold water, and the third very soluble. The first is *dimethyldicyanomethyl-3-methylbenzidine*, m. p. 93—94°; the second is a quaternary *iodide* of the formula

$$CN\cdot CH_2\cdot NMe\cdot C_6H_3Me\cdot C_6H_4\cdot NMe_3I,$$

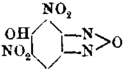
m. p. 145—148°; and the third is the diquaternary *di-iodide* of the original base, $I\cdot NMe_3\cdot C_6H_4\cdot C_6H_3Me\cdot NMe_3I$, m. p. 155°.

J. C. W.

Nitro-derivatives of *iso*Oxadiazole Oxides and of *iso*Oxadiazoles. Arthur G. Green and Frederick Maurice Rowe (T., 1918, **113**, 67—74. Compare T., 1913, **103**, 2025).—Attention has already been directed to the acidic nature of 4:6-dinitrobenzisooxadiazole oxide. This acidity is either to be attributed to the

hydrogen atom at position 5, or possibly the compound is really 4 : 6-dinitro-5-hydroxybenz*iso*oxadiazole, thus:

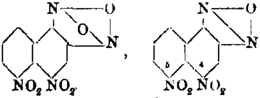
or



(I.) (II.)

A compound of the formula (I) *would require* 20 *atoms of hydrogen* per molecule for reduction, whilst a substance of the alternate type (II) would absorb 18 atoms. As a matter of fact, it is found on titration with titanous chloride that 20 atoms are used.

Nitro-derivatives of naphth*iso*oxadiazole and its oxide (A., 1917, i, 518) have been prepared. They probably have the formulæ



and (4, and 5) $NO_2\cdot C_{10}H_5<^N_N>O$

For experimental details, see the original. J. C. W.

Mechanism of the Coupling Reaction. OTTO DIMROTH, HELMUT LEICHTLIN, and OTTO FRIEDEMANN (*Ber.*, 1917, **50**, 1534—1548).—The first stage in the coupling of a diazonium salt with a phenol was supposed by Dimroth to consist in the formation of a diazo-ether, which would subsequently undergo rearrangement into the ordinary azo-compound. It was found, for example, that *p*-nitrophenol and *p*-bromobenzene-diazonium chloride gave an unstable intermediate compound of the constitution $NO_2\cdot C_6H_4\cdot O\cdot N_2\cdot C_6H_4Br$, which changed into the normal compound, $NO_2\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_4Br$ (A., 1907, i, 662). Two criticisms of this theory have appeared. One is based on the fact that phenolic ethers also form azo-compounds, which has led to the view that addition of the diazonium compound takes place at the conjugated double linkings (Meyer and others, A., 1914, i, 882). On the other hand, Auwers has suggested that the first products are not ethers, $R\cdot O\cdot N\colon N\cdot R'$, but diazonium salts, $R\cdot O\cdot NR'\vdots N$ (A., 1915, i, 85). An answer to the second criticism is now given.

Morgan and Wootton's stable diazonium salts, 4-benzoylamino-naphthalene-1-diazonium chloride and *p*-acetylaminobenzene-diazonium chloride, have been treated with phenols ranging in strength from picric acid to pentamethylphenol. The molecular conductivities of the products in 80% acetone at 0° have been measured, and the results show that the compounds with picric acid and dinitrophenol are true diazonium salts with the same conductivities as the chlorides or trichloroacetates, whereas the weaker phenols and enols give true ethers with conductivities as low as that of *p*-nitrobenzeneazomethyl ether.

Benzoyl-1 : 4-naphthalenediamine is obtained from the 4-nitro-

compound by a slight modification of Morgan's method (T., 1907, **91**, 1316) and converted into the diazonium chloride. This reacts with dilute sodium hydroxide to form, not the nitrosoamine, $NHBz\cdot C_{10}H_6\cdot NH\cdot NO$, as Morgan supposed, but the *quinonediazide*, $NBz:C_{10}H_6<\overset{N}{\underset{N}{\vdots}}$, which crystallises from diluted acetone as a brownish-yellow substance. 4-*Benzoylaminonaphthalene*-1-*diazonium trichloroacetate*, m. p. 124° (decomp.), *picrate*, m. p. 141—142°, and 2:4-*dinitrophenoxide*, m. p. 75° (decomp.), are prepared by precipitation from the chloride and the acid or phenol, with or without the addition of sodium acetate. The diazonium chloride couples with *p*-nitrophenol to form 4-*benzoylaminonaphthalene*-1-*azo*-p-*nitrophenyl ether*,

$$NHBz\cdot C_{10}H_6\cdot N:N\cdot O\cdot C_6H_4\cdot NO_2,$$

m. p. 115—120° (decomp.), which has a somewhat higher conductivity than the other diazo-ethers. The enolic form of dibenzoylacetylmethane yields 4-*benzoylaminonaphthalene*-1-*azo*-*aa*-*dibenzoyl*-*β*-Δ^a-*propenyl ether*, $NHBz\cdot C_{10}H_6\cdot N:N\cdot O\cdot CMe:CBz_2$, m. p. 134—135°; this is completely hydrolysed by ethereal hydrochloric acid only after some hours, the components being formed on the one hand, and acetyl chloride and the *compound*,

$$NHBz\cdot C_{10}H_6\cdot NH\cdot N:CBz_2,$$

brownish-yellow crystals, m. p. 225°, on the other. p-*Acetylaminobenzeneazo*-*aa*-*dibenzoyl*-*β*-Δ^a-*propenyl ether* forms large, yellow crystals, m. p. 145—146°.

For the preparation of pentamethylphenol, *s.*-*m*-xylidine hydrochloride is heated with methyl alcohol at 250°, and the pentamethylaniline is diazotised. Pentamethylphenol is so feebly acidic that the alternative quinonoid formula has to be considered, thus: $H\cdot C_6Me_5:O \longrightarrow C_6Me_5\cdot OH$. It dissolves more freely in alkalis than in water (1 litre of boiling water dissolves 1·5 grams; 1 litre of boiling 0·8*N*-potassium hydroxide dissolves 12 grams), but the free phenol, and not the salt, crystallises from saturated solutions. Furthermore, the conductivity of a mixture of the phenol and sodium hydroxide in 50% alcohol does not vary with time. The phenol is therefore not an enolisable ketone, but a true, but very weak, hydroxy-compound, comparable with amyl alcohol.

Benzeneazo pentamethylphenyl ether, $C_6Me_5\cdot O\cdot N:NPh$, is a very unstable, brownish-yellow substance, which may even explode spontaneously at the ordinary temperature. 4-*Benzoylaminonaphthalene*-1-*azo pentamethylphenyl ether* is quite harmless to handle, but the pale yellow granules explode at 81°. p-*Acetylaminobenzeneazo pentamethylphenyl ether* is a straw-yellow powder which detonates at 69°.

Mesitol and *iso*durenol also give precipitates of diazo-ethers when mixed with neutralised diazonium salt solutions of the above types, but the products decompose before they can be dried. [See also *J. Soc. Chem. Ind.*, 1918, 118A.] J. C. W.

Swelling of Fibrin in Polybasic Acids and their Salts. MARTIN H. FISCHER and MARTIN BENZINGER (*J. Amer. Chem. Soc.*, 1918, **40**, 292—303).—Experiments on the absorption of

water by fibrin in acid and alkaline solutions containing the acid salts (using phosphoric and citric acids) gave essentially the same results as when gelatin was used (see below), with the exception that the points of minimum absorption corresponded with a different acid content in the solution. [See also *J. Soc. Chem. Ind.*, 1918, 131A.] L. A. C.

Preparation of Plant Nucleic Acids. GEORGE CLARKE and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1917, **11**, 319—324).—Nucleic acid is extracted from plant tissues by 10% sodium chloride solution *in the form of nucleates of proteins, and is precipitated* in this form from the extract by hydrochloric acid. If the plant material is first boiled with strong alcohol, subsequent extraction with salt solution and precipitation with acid yields a product free *from proteins. Methods for the preparation of nucleic acid from* yeast and from wheat embryos are described. The purified products from both sources contain the proportions of nitrogen and phosphorus required by Levene's formula, $C_{38}H_{50}O_{29}N_{15}P_4$ (A., 1909, i, 541). [See also *J. Soc. Chem. Ind.*, 1918, March.] J. H. L.

Structure of Yeast-nucleic Acid. II. Uridinephosphoric Acid. P. A. LEVENE (*J. Biol. Chem.*, 1918, **33**, 229—234. Compare Levene, A., 1917, i, 670).—The previously described cytosine–uracil–dinucleotide is now shown to be a mixture of the two simple mononucleotides, the brucine salts of which can be separated by fractional crystallisation from 35% alcohol. The less soluble fraction consists of *brucine uridinephosphate*, $C_{55}H_{63}O_7N_6P,7H_2O$, which contracts at 183°, then melts, and finally decomposes at 198° (corr.). It is converted into the *barium* salt, $C_9H_{11}O_9N_2PBa$, crystallising from water in rosettes of long needles, $[\alpha]_D^{20}+3.5°$, in a 2·5% solution of hydrochloric acid. After hydrolysis, the only pyrimidine which can be detected is uracil.

The more soluble fraction consists of *brucine cytidinephosphate*, but the corresponding barium salt has not yet been obtained in a crystalline form. In the light of these results, the presence of a tetraribose nucleus in yeast-nucleic acid (see Jones and Read, A., 1917, i, 233) cannot yet be regarded as established. H. W. B.

Swelling of Gelatin in Polybasic Acids and their Salts. MARTIN H. FISCHER and MARIAN O. HOOKER (*J. Amer. Chem. Soc.*, 1918, **40**, 272—292).—The absorption of water by gelatin was determined in different concentrations of the primary, binary, and ternary salts of phosphoric, citric, and carbonic acids, and in solutions varying from pure acid to pure alkali (sodium hydroxide) for the same three acids. The absorption is greatest in pure acids and alkali, decreasing considerably in the presence of salts, and with certain salts at high concentrations is less than in pure water. From a certain minimum there is a progressive increase in the absorption with increase of the acid or alkali content of the mixture. The results are held to be applicable to absorption by proto-

plasm in living cells, there being increased turgor or œdema with every increase in the acid or alkali content of the cell, even in the presence of "buffer" salts. [See also *J. Soc. Chem. Ind.*, 1918, 131A.] L. A. C.

The Liquefaction or "Solution" of Gelatin in Polybasic Acids and their Salts. MARTIN H. FISCHER and WARD D. COFFMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 303—312).—Experiments showed that there is a progressive increase in the tendency of gelatin to go into solution in mixtures of the salts of polybasic acids as the amount of acid or alkali in these mixtures is increased from a given low point. This shows that hydration and "solution" of a protein are not the same thing, for if they were, the addition of an acid or an alkali to a solution should cause it to gel, for this causes increased hydration (see previous abstracts). The results have an important bearing on many physiological problems, such as acid intoxication, digestion, etc. [See also *J. Soc. Chem. Ind.*, 1918, 131A.] L. A. C.

Chemical Composition and Biological Availability of Peptone. L. DAVIS (*J. Lab. Clin. Med. St. Louis*, 1917, **3**, 75—86; from *Physiol. Abstr.*, 1918, **2**, 662).—A comparison of domestic peptones with Witte's product. It is most important to determine the products of hydrolysis, physical properties and elementary chemical analysis being secondary to this. Tyrosine and tryptophan are important constituents. The best comparison is given by quantitative biochemical tests, such as the elaboration of diphtheria and tetanus toxins and the production of indole. Domestic peptones do not give a potent diphtheria toxin, although furnishing good tetanus toxin and frequently yielding indole.

W. G.

The Surface Tension of Solutions of Ferments. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 50—58).—Stalagmometric measurements of solutions of various enzymes. S. B. S.

The "Reversion of Diastatic Action." L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 37—41).—The amount of starch precipitated when its solutions are treated with diastase depends on their previous treatment. If soluble starch solutions of varying concentrations are treated with the same amount of diastase, it will be found that within a given time starch precipitation will appear first in lower concentrations of those solutions which have been cooled before being submitted to the ferment (at the ordinary temperature), and in higher concentrations of solutions which have been heated. The action of the diastase is ascribed by the author to the aggregation of colloidal particles. The action of diastase diminishes the viscosity, and thus promotes the precipitation of the larger particles as they are formed. The cooled solution of starch will, before treatment with diastase, contain more of the larger

aggregates than the heated solution. [See also *J. Soc. Chem. Ind.*, 1918, 133A.] S. B. S.

Action of Oxidising and Reducing Substances on Diastases. L. BERCZELLER and E. FODOR (*Biochem. Zeitsch.*, 1917, **84**, 42—49).—Potassium permanganate, hydrogen peroxide, and iodine in very small concentrations inhibit the action of diastase. Ordinary formaldehyde ("formalin") accelerates slightly the diastatic action, but this acceleration is due to the formic acid it contains. If neutralised, it has a slight inhibitory action. S. B. S.

Enzyme Action. XVI. Formation of Ester-hydrolysing Substances by the Action of Alkali on Proteins. FLORENCE HULTON-FRANKEL (*J. Biol. Chem.*, 1917, **32**, 395—407. Compare Falk, A., 1917, i, 598).—Proteins (caseinogen, gelatin, etc.) are shaken with alkali solutions, and after twenty-four hours the turbid liquids are treated with hydrochloric acid until only a slightly alkaline reaction is obtained. Portions then incubated with ethyl butyrate or other esters cause a distinctly greater hydrolysis to occur than is observed in control solutions of the same hydroxyl-ion concentration. The most active solutions are obtained when the concentration of the alkali acting on the protein is about $3N$. Raising the temperature to 80° increases the activity of the resulting lipolytic solution. When treated with acid instead of alkali, the protein solutions are devoid of ester-hydrolysing properties. Dialysis only partly removes the lipolytic property of the alkali-protein solutions, whilst boiling does not exert the slightest inactivating action. [See, further, *J. Soc. Chem. Ind.*, 1918, 135A.] H. W. B.

The Preparation of Urease from Bacteria. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **84**, 354—357).—The bacteria are removed from the culture on agar and dried on porous porcelain. A preparation is thus obtained which can be preserved for a long time, and is active in the presence of toluene. S. B. S.

The Formation of Ferments. V. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **84**, 358).—The addition of leucine does not increase the activity of the permanent urease preparation (see preceding abstract), but rather inhibits it. This fact indicates, taken in conjunction with the author's previous work, that this amino-acid is necessary for the formation of the enzyme, but has no effect on its activity. S. B. S.

Silicon-Hydrocarbons with Nuclei containing Halogens, and their Use in Syntheses. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, **50**, 1559—1568).—*p*-Chlorobromo- and *p*-dibromo-benzene react with magnesium to form the magnesium *p*-halogenophenyl bromides. When these are treated with silicon tetrachloride, they yield the trichloro-*p*-halogenophenylmonosilanes, $SiCl_3 \cdot C_6H_4X$, which react with magnesium alkyl haloids to form *p*-halogenophenyltrialkylmonosilanes. Compounds of this type

react most readily with magnesium, but not very smoothly with sodium, but they may be applied very extensively in Grignard and Fittig syntheses. Some very unusual examples are now described.

Magnesium *p*-bromophenyl bromide and silicon tetrachloride yield *trichloro*-p-*bromophenylmonosilane* (p-*bromophenylsilicon trichloride*), a colourless oil, b. p. 120—125°/15 mm., which is immediately hydrolysed by water to p-*bromophenylsilicic acid* ("*hydroxyoxo*-p-*bromophenylmonosilane*," according to Stock's nomenclature), $C_6H_4Br \cdot SiO \cdot OH$, a white powder, and also *dichlorodi*-p-*bromophenylmonosilane*, $SiCl_2(C_6H_4Br)_2$, snow-white prisms, m. p. 60°, b. p. 238—240°/21 mm. The trichloride reacts with magnesium ethyl bromide to form p-*bromophenyltriethylmonosilane*,

$$SiEt_3 \cdot C_6H_4Br,$$

b. p. 149°/14 mm., D_4^{21} 1·1643 n_{H_α} 1·52836, n_D 1·53280, $n_{H\beta}$ 1·54411, n_{H_γ} 1·55395, at 21°.

From *p*-chlorobromobenzene, the following compounds may be obtained by the same reactions. *Trichloro*-p-*chlorophenylmonosilane*, b. p. 105°/15 mm.; p-*chlorophenylsilicic acid*, a colourless powder; p-*chlorophenyltriethylmonosilane*, b. p. 261—262°/760 mm., 137°/14·5 mm., $D_4^{9.6}$ 1·0056, n_{H_α} 1·51777, n_D 1·52193, $n_{H\beta}$ 1·53255, n_{H_γ} 1·54168, at 9·6°; p-*chlorophenyltri*-n-*propylmonosilane*, b. p. 160°/14 mm., D_4^9 0·9708, n_{H_α} 1·50835, n_D 1·51234, $n_{H\beta}$ 1·52225, n_{H_γ} 1·53059, at 9°.

p-Bromophenyltriethylmonosilane reacts readily with magnesium that has been etched by iodine to give the organo-magnesium compound in about 90% yield. This is ascertained from the weight of phenyltriethylmonosilane, b. p. 230—240°, left on decomposing the compound with water. The following products have been obtained from the magnesium compound: by means of iodine, p-*iodophenyltriethylmonosilane*, a colourless liquid, b. p. 165°/13 mm., D_4^{20} 1·3304, n_{H_α} 1·55711, n_D 1·56233, $n_{H\beta}$ 1·57578, n_{H_γ} 1·58709, at 20°; with lead trimethyl bromide, p-*triethylsilyltrimethylplumbylbenzene*, $SiEt_3 \cdot C_6H_4 \cdot PbMe_3$, a stable, viscous oil, b. p. 191°/17 mm., D_4^{23} 1·3997, n_{H_α} 1·54379, n_D 1·54937, $n_{H\beta}$ 1·56240, n_{H_γ} 1·57417, at 23·8°, which is resolved by bromine at −75° into lead trimethyl bromide and *p*-bromophenyltriethylmonosilane; by means of tin triethyl bromide, p-*triethylsilyltriethylstannylbenzene*, $SiEt_3 \cdot C_6H_4 \cdot SnEt_3$, a colourless, viscous oil, b. p. 214°/18 mm., $D_4^{21.2}$ 1·1216, n_{H_α} 1·52316, n_D 1·52756, $n_{H\beta}$ 1·53888, n_{H_γ} 1·54864, at 21·2°.

p-Chlorophenyltriethylmonosilane reacts with chlorodiphenylarsine in the presence of sodium to form p-*diphenylarsyltriethylsilylbenzene*, $SiEt_3 \cdot C_6H_4 \cdot AsPh_2$, as a colourless, viscous oil, b. p. 279—281°/17 mm., $D_4^{21.3}$ 1·1661, n_{H_α} 1·60784, n_D 1·61455, $n_{H\beta}$ 1·63181, n_{H_γ} 1·64718, at 21·3°, which forms crystalline *additive* compounds with mercuric salts (*chloride*, m. p. 188°; *bromide*, m. p. 181°; *iodide*, m. p. 139·5°).

From the optical data, the molecular refractions and dispersions of the above *p*-halogenophenyltrialkylmonosilanes have been calculated, and the atomic refractions and dispersions of the silicon atom have been worked out. These are tabulated with Bygdén's

values for phenyltriethylmonosilane (A., 1915, ii, 809), and it obvious that the contribution of the silicon atom rises with th mass of the groups attached to it.

All densities are reduced to vacuum standard. J. C. W.

Benzyltrimethylsilicane-*p*-sulphonic Acid and some of it Derivatives. ARTHUR BYGDÉN (*J. pr. Chem.*, 1917, [ii], 96 86—104).—Benzyltrimethylsilicane (Bygdén, A., 1912, i, 341) ca be fairly easily converted into a sulphonic acid which, unlike mo of the organic silicane sulphonic acids described previously, easily isolated and convertible into crystalline salts.

When treated in chloroform solution with an equimolecula quantity of chlorosulphonic acid, benzyltrimethylsilicane yiel *benzyltrimethylsilicane-p-sulphonic acid*, $SiMe_3\cdot CH_2\cdot C_6H_4\cdot SO_3H$ rectangular tablets with $2H_2O$, which melt in their water of crysta lisation at 99—114°; the monohydrated acid has m. p. 116·0—116·5°; the position of the sulphonic acid group is demonstrate by the formation of *p*-hydroxybenzoic acid on fusing with potassiu hydroxide and of toluene-*p*-sulphonic acid on boiling with aqueou potassium hydroxide. The following salts were prepared *potassium* salt, rectangular or rhombic leaflets with $1H_2O$ *rubidium* salt, rectangular leaflets with $1H_2O$; *caesium* sal hexagonal leaflets with $\frac{1}{2}H_2O$; *sodium* salt, leaflets with $2H_2O$ *lithium* salt, crystals with $2H_2O$; *calcium* salt, rhombic tablets wit $2H_2O$; *strontium* salt, needles with $2H_2O$; *barium* salt, needl with $2H_2O$; *magnesium* salt, rhombic leaflets with $7\frac{1}{2}H_2O$; *zin* salt, platelets or needles with $6H_2O$; *cadmium* salt, platelets o needles with $6H_2O$; *ferrous* salt, almost colourless leaflets wit $7H_2O$; *nickel* salt, green leaflets or needles with $7H_2O$; *cobalt* sal red leaflets with $8H_2O$; *lead* salt, needles with $2H_2O$; *copper* sal blue leaflets with $6H_2O$; *silver* salt, rectangular leaflets with $2H_2O$ *ammonium* salt, tablets with $1H_2O$; *methylammonium* sal elongated tablets, m. p. 144—172°; *ethylammonium* salt, leaflet prisms, or tablets, m. p. 110·5—111·5° (corr.); *brucine* sal rhombic tablets, m. p. 215·5—217·5° (corr.). The potassium sa of the sulphonic acid on treatment with phosphorus pentachlori yielded *benzyltrimethylsilicane-p-sulphonyl chloride*,

$$SiMe_3\cdot CH_2\cdot C_6H_4\cdot SO_2Cl,$$

tablets, m. p. 45·5—46·5° (corr.), and the corresponding *bromid* $SiMe_3\cdot CH_2\cdot C_6H_4\cdot SO_2Br$, rectangular tablets, m. p. 60—60·5 (corr.), was obtained in a similar manner with the use of pho phorus pentabromide. By allowing the acid chloride to react i ethereal solution with various bases, *benzyltrimethylsilicane-p-sulphonamide*, $SiMe_3\cdot CH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$, tablets or prisms, m. p 81—81·5° (corr.), and the corresponding *methylamide*, prism m. p. 76·4—77·2° (corr.), *benzylamide*, leaflets, m. p. 130·5—131 (corr.), *anilide*, hexagonal or rhombic tablets, m. p. 124·2—125 (corr.), *methylanilide*, needles, m. p. 71·5—72·5° (corr.), *o-toluidid* tablets, m. p. 153—153·5° (corr.), and *p-toluidide*, rhombic tablet m. p. 97—98° (corr.), were also prepared. D. F. T.

New Heterocyclic Systems. IV. Dimethyl- and Diethyl-*cyclo*pentamethylenestannine and their Scission Products. GERHARD GRÜTTNER, ERICH KRAUSE, and MAXIMILIAN WIERNIK (*Ber.*, 1917, **50**, 1549—1558. Compare A., 1917, i, 122).—Cyclic compounds containing five carbon atoms and one tin atom in the ring have now been obtained by methods analogous to those employed in the case of lead.

Tin diethyl dibromide, which is readily prepared by heating tin filings with ethyl bromide at 175—180°, reacts with the magnesium compound of αε-dichloropentane to form *diethyl*cyclo*pentamethylenestannine*, C_5H_{10}:$SnEt_2$, which is a colourless, mobile oil, with the odour of fir-needle extract, and has b. p. 95°/14 mm., $D_4^{19.9}$ 1·2693, n_{H_α} 1·50298, n_D 1·50673, n_{H_β} 1·51586, n_{H_γ} 1·52357, at 19·9°. The oil is stable in the absence of air, but otherwise it gradually deposits a white resin. The ring is opened by means of bromine, diluted with ethyl acetate, at 0°, when *tin diethyl-ε-bromoamyl bromide*,

$C_5H_{10}Br \cdot SnEt_2Br$,

is formed as a very viscous oil, b. p. 190·5°/16 mm., D_4^{20} 1·7113, n_{H_α} 1·54270, n_D 1·54707, n_{H_β} 1·55768, n_{H_γ} 1·56675, at 20·3°. This reacts with magnesium ethyl bromide to form *tin triethyl-ε-bromoamyl*,

$SnEt_3 \cdot C_5H_{10}Br$,

which is a stable, almost odourless, mobile oil, b. p. 155·5°/15 mm., D_4^{20} 1·3723, n_{H_α} 1·50204, n_D 1·50563, n_{H_β} 1·51457, n_{H_γ} 1·52213, at 19·1°. The halogen is removed from this substance by converting it into its magnesium compound and decomposing this with water; the main product is *tin triethyl-*n*-amyl*, b. p. 110°/15 mm., D_4^{20} 1·1258, n_{H_α} 1·47070, n_D 1·47400, n_{H_β} 1·48216, n_{H_γ} 1·48904, at 20°, but there is formed as well some *ακ-hexaethyldistannyldecane*,

$SnEt_3 \cdot [CH_2]_{10} \cdot SnEt_3$,

which distils without decomposition, and has b. p. 248°/15 mm., $D_4^{20.7}$ 1·1887, n_{H_α} 1·49480, n_D 1·49835, n_{H_β} 1·50687, n_{H_γ} 1·51421, at 20·7°. *Tin diethyl-*n*-amyl bromide*, $C_5H_{11} \cdot SnEt_2Br$, an unpleasant-smelling, viscous oil, b. p. 135°/15 mm., $D_4^{22.3}$ 1·4365, n_{H_α} 1·50484, n_D 1·50866, n_{H_β} 1·51825, n_{H_γ} 1·52657, at 22·3°, is formed by the action of bromine on the tin tetra-alkyl.

*Dimethyl*cyclo*pentamethylenestannine* is obtained from tin dimethyl di-iodide, as above; it closely resembles the homologue, and has b. p. 64°/16 mm., $D_4^{23.1}$ 1·3357, n_{H_α} 1·49861, n_D 1·50242, n_{H_β} 1·51184, n_{H_γ} 1·51993, at 23·1°. *Tin dimethyl-ε-bromoamyl bromide* has b. p. 168°/14·5 mm., D_4^{24} 1·8385, n_{H_α} 1·54548, n_D 1·54983, n_{H_β} 1·56085, n_{H_γ} 1·57019, at 24°, and *tin trimethyl-ε-bromoamyl* has b. p. 124°/18 mm., $D_4^{23.4}$ 1·4659, n_{H_α} 1·49604, n_D 1·49976, n_{H_β} 1·50895, n_{H_γ} 1·51677, at 23·4°. The magnesium compound of the latter reacts with lead trimethyl bromide to form *α-trimethylstannyl-ε-trimethylplumbylpentane*, $SnMe_3 \cdot [CH_2]_5 \cdot PbMe_3$, as a colourless, viscous oil, b. p. 162°/17·5 mm., $D_4^{23.2}$ 1·6482, n_{H_α} 1·51822, n_D 1·52282, n_{H_β} 1·53452, n_{H_γ} 1·54473, at 23·2°.

Tin triethyl bromide reacts with the magnesium compound of αε-dichloropentane to form *αε-hexaethyldistannylpentane*, b. p. 205·5°/14·5 mm., D_4^{20} 1·2654, n_D^{20} 1·5053, $n_\gamma - n_C$ 0·01312.

Similarly, lead trimethyl bromide gives *αε-hexamethyldiplumbyl-*

pentane, $PbMe\cdot[CH_2]_5\cdot PbMe_3$, b. p. 166·5°/14 mm., $D_4^{23·9}$ 1·9448, $n_D^{23·6}$ 1·5571, $n_F - n_C$ 0·01940.

All the densities are reduced to vacuum standard, and in many cases sets of refractive indices at higher temperatures are recorded.

J. C. W.

Physiological Chemistry.

Applications of Gas Analysis. III. Apparatus for the Study of the Respiratory Exchange in Small Animals. A. L. PRINCE (*J. Biol. Chem.*, 1917, **32**, 333—336).—The apparatus described is suitable for the study of the respiratory exchange in rats and similar animals and for teaching purposes. H. W. B.

Applications of Gas Analysis. VI. Respiratory Exchange and Indirect Calorimetry. YANDELL HENDERSON (*J. Biol. Chem.*, 1918, **33**, 47—53).—A simple spirometer is described which permits the measurement of the expired air and the analysis of a sample of it by the methods previously detailed (see this vol., ii, 81). Directions for the calculation of the respiratory quotient and exchange are appended. H. W. B.

Applications of Gas Analysis. II. Carbon Dioxide Tension of the Venous Blood and the Circulation Rate. YANDELL HENDERSON and A. L. PRINCE (*J. Biol. Chem.*, 1917, **32**, 325—331. Compare A., 1917, ii, 506).—The authors describe a simple method for estimating the carbon dioxide tension of venous blood. The subject makes the deepest possible expiration into an empty rubber bag. After a few minutes, the expired air is inhaled, and after being retained for ten seconds in the lungs is again expired into the bag. This procedure is repeated at intervals five or six times, and then the estimation of the percentage of carbon dioxide gives the required carbon dioxide tension of the venous blood of the patient. H. W. B.

Relationship between Cholesterol and Cholesterol Esters in the Blood during Fat Absorption. ARTHUR KNUDSON (*J. Biol. Chem.*, 1917, **32**, 337—346. Compare Bloor, A., 1916, i, 450; Bloor and Knudson, A., 1917, i, 236).—During fat absorption in dogs, the cholesterol in the blood remains unchanged, but the amount of cholesterol esters in both plasma and corpuscles increases, the increase being most marked in the corpuscles. Similar changes are observed in the lecithin and total fatty acids of the plasma and corpuscles; indeed, a fairly constant relationship between lecithin, cholesterol esters, and total fatty acids in the blood is noted. The blood corpuscles evidently play a very important part in fat metabolism. H. W. B.

The Amount and the Distribution of Creatine and Creatinine in Normal Human Blood. ANDREW HUNTER and WALTER R. CAMPBELL (*J. Biol. Chem.*, 1918, **33**, 169—191).—The amount of creatinine in normal human blood plasma ranges under different conditions from 0·7 to 1·3 mg. per 100 c.c., average 1 mg., and it is practically certain that it is distributed through corpuscles and plasma in uniform concentration. It is apt to be lower in the female than in the male, and lower in sedentary than in active subjects.

Creatine is chiefly concentrated in the corpuscles; roughly, it may be said that corpuscles contain 6 to 9 mg. per 100 c.c., whilst plasma contains but 0·4 to 0·6 mg. The blood as a whole seems, on an average, to contain about 3 mg. per 100 c.c. There seems to be more in the blood of females than in that of males.

There is a distinct correspondence between increase of plasma creatine and the appearance of creatine in the urine. A. J. G.

Amino-nitrogen and Dextrose in Lymph and Blood before and after the Injection of Nutrient Solutions in the Intestine. BYRON M. HENDRIX and JOSHUA E. SWEET (*J. Biol. Chem.*, 1917, **32**, 299—307).—In a fasting dog, the thoracic lymph contains less amino-nitrogen but more dextrose than the blood. After the injection of milk, peptone, or amino-acid solutions into the intestine, the amino-nitrogen in both the blood and the lymph increases, but the amount in the lymph is greater than in the blood. The introduction of sugar solutions into the intestine is followed similarly by a large increase in the dextrose content of the lymph and a smaller rise of the dextrose in the blood of the general circulation. In some cases the dextrose in the lymph approximates in amount to that present in the mesenteric veins. The authors suggest that absorption of dextrose and amino-acids takes place into both lymph and blood, but as the volume and rate of flow of the blood are so much greater than those of the lymph, the concentration of dextrose and amino-acid attained in the former is correspondingly less than in the latter fluid. H. W. B.

Use of Indicators for the Colorimetric Determination of the Hydrogen-ion Concentration of Sera. ANNIE HOMER (*Biochem. J.*, 1917, **11**, 283—291).—Six out of fifteen indicators examined can be applied to the colorimetric determination of hydrion concentration in sera, using the Walpole colorimeter. Neutral red gives accurate results over the range $p_H = 5·9—7·6$, whilst dibromo-*o*-cresolsulphonephthalein is satisfactory for $p_H = 5·2—5·4$, and tetrabromophenolsulphonephthalein for $p_H = 3·0$. α-Naphtholphthalein, phenolsulphonephthalein, and dibromothymolsulphonephthalein, the respective ranges of which are $p_H = 7·6—8·5$, $6·8—8·4$, and $6·0—7·6$ in pure solutions, indicate consistently low values of p_H (that is, high acidities) when used with sera, but as the differences are fairly constant for sera containing 4—10% of protein, and as a rule do not exceed one unit, these indicators can be employed in routine work if suitable correc-

tions are made. Each operator should determine the necessary corrections by making comparative determinations of p_H on the same sera colorimetrically and electrometrically. By the colorimetric method, it is possible to determine rapidly the amount of acid or alkali required to adjust the reaction of a serum to any given value within the usefnl range of any of the indicators mentioned, and also, by interpolation, to certain intermediate values not amenable to direct colorimetric observation. J. H. L.

Influence of the Heat Denaturation of ψ-Globulin and Albumin on the Nature of the Protein appearing in Concentrated Sera. ANNIE HOMER (*Biochem. J.*, 1917, **11**, 292—306).—The extent of the denaturation of the proteins in antitoxic sera at 57·5° (compare A., 1916, i, 614; 1917, i, 497), as measured by their increased precipitability by ammonium sulphate at 30% of saturation, attains its maximum after four hours' heating when the reaction of the liquid is alkaline, but after only one hour when the reaction is acid; the nature of the changes involved appears to be different in the two cases. Tables and curves are given showing the influence of hydrion concentrations between $p_H = 9·5$ and 4·5 on the denaturation of albumin and ψ-globulin when their aqueous solutions are heated for six hours at 57·5°. Further tables show the precipitating power of various concentrations of ammonium sulphate with respect to solutions of albumin and ψ-globulin, of reaction $p_H = 8$, before and after heating for six hours at 57·5°. From the observations made, it is concluded that in the concentration of antitoxic sera by methods involving thermal denaturation of the proteins, the preliminary heating at 57·5° should be continued for four to five hours if the reaction of the serum is on the alkaline side of $p_H = 7$. By employing ammonium sulphate at 44% instead of 50% of saturation for the precipitation of the second fraction from thermally denaturated sera, complete precipitation of the ψ-globulin (and therefore of the antitoxin) is attained, whilst the proportion of albumin appearing in the second fraction is considerably reduced. The final product is thereby rendered lighter in colour and more potent. J. H. L.

The Formation of Lactose from Starch by the "Loosened" Ferments of Sucrose Serum. F. RÖHMANN (*Biochem. Zeitsch.* 1917, **84**, 399—401).—The parenteral injection of sucrose into rabbits gives rise to special ferments in the serum ("hervorgelockte Fermente"). The extract of the liver of a rabbit thus treated acts on soluble starch, causing degradation and producing, amongst other products, lactose. S. B. S.

Occurrence of Lichenase in the Digestive Tract of Invertebrates. MINNA E. JEWELL and HOWARD B. LEWIS (*J. Biol. Chem.*, 1918, **33**, 161—167).—Lichenin, the complex carbohydrate in Iceland moss, is readily hydrolysed by the enzyme lichenase, which is found in various invertebrates, but not in vertebrates. The enzyme occurs usually in the pancreas, but in smaller animals

the alimentary tract may be taken as a whole for the preparation of the enzymic extract. The behaviour of the pancreatic extract to lichenin constitutes therefore a chemical method of differentiating between vertebrate and invertebrate animals. H. W. B.

The Inter-relation of the Surviving Heart and Pancreas of the Dog in Sugar Metabolism. A. H. CLARK (*J. Exp. Med.*, 1917, **26**, 721—724; from *Physiol. Abstr.*, 1918, **2**, 678—679).—When the pancreas of a dog is perfused aseptically with Locke's solution containing physiological concentration of dextrose, the optical rotation of the perfusate is diminished, but its reducing power is unaltered. Similar results are obtained when a mixture of dextrose and sugar-free pancreatic perfusate is incubated, and the osazones from these perfusates have lower *m. p.*'s than glucosazone. When a pancreatic perfusate containing dextrose is circulated through the living heart, the above changes occur, and in addition the reducing properties of the perfusate are altered. These phenomena are believed to be due to an enzyme or enzymes obtained from the perfused pancreas. It is suggested that these enzymes have a specific action on dextrose, lævulose being unchanged when perfused, and that they are responsible for the preparation of that sugar for normal utilisation. Nothing definite can be stated as to the degree of condensation produced or the nature of the polysaccharides formed. W. G.

Influence of Thyroid-feeding on Carbohydrate Metabolism. I. Storage and Mobilisation of the Liver Glycogen in Thyroid-fed Animals. II. Amount of Adrenaline in the Adrenals of Thyroid-fed Rats. III. Acidosis in Experimental Hyperthyroidism and its Relation to Adrenaline in the Blood and the Decrease of Liver Glycogen. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **33**, 193—205, 207—213, 215—227).—Feeding an animal with thyroid gland causes a rapid disappearance of glycogen from the liver. The author now shows that a formation of glycogen in the liver of an animal fed on thyroid gland and carbohydrate occurs only when the amount of carbohydrate administered is exceedingly large. The increased diastatic activity of the liver which these results indicate may be due to the acidosis which is likewise induced by feeding with thyroid gland, although the simultaneous administration of sodium hydrogen carbonate fails to depress the diastatic activity as it does in the normal animal. There does not seem to be any connexion between hyperthyroidism and excessive activity of the adrenals. The amount of adrenaline in the adrenals of animals fed with thyroid gland is not greater than in those of normal animals; the glands are also not increased in size. H. W. B.

Nutritive Factors in Animal Tissues. I. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1917, **32**, 309—323).—Preparations of muscle (meat extract, meat powder, etc.) contain

protein suitable for nutritional purposes, but are unable to promote the growth of rats, owing to a lack of the water-soluble vitamine. Dried pig's liver contains both protein and vitamine, and charts are given which depict the rapid growth which occurs when this material is the sole source of protein in the diet.

H. W. B.

Composition and Digestive Activity of Different Fractions of the Pancreas. II. R. A. NELSON and J. H. LONG (*J. Amer. Chem. Soc.*, 1917, **39**, 1766—1778. Compare A., 1915, i, 1025) —A more complete account of the distribution of the enzymes in the three layers into which minced pancreas can be separated by centrifugation at a very high speed. Amylopsin is mostly found in the middle, liquid layer, which is more active than the non-centrifuged pancreas; trypsin is found in all the fractions, but chiefly in the solid ones; lipase and esterase are mainly present in the solid layers. The pancreas of the hog, compared with that of the ox or sheep, is chiefly remarkable for the enormous amylolytic activity of its liquid layer, whilst it also exceeds these in lipolytic power. The proportions of fatty, liquid, and protein layers in the three cases are also recorded, and analyses given of the soluble solids found in the liquid layer. J. C. W.

The Physical Chemistry of Cell Membranes. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 59—74).—The tendency of substances to accumulate at the surface of cells is discussed in connexion with the surface tension of solutions. Stalagmometric measurements of extracts of organs are given. S. B. S.

The Action of Animal Tissue on Methylene-blue. T. THUNBERG (*Skand. Arch. Physiol.*, 1917, **35**, 163—195; from *Physiol. Abstr.*, 1918, **2**, 655).—A detailed study of the dehydrogenation of succinic acid by "dehydrogenase" and methylene-blue, and a full theoretical discussion of the reaction (compare this vol., ii, 87). W. G.

Theory of the Biochemical Action of Light. C. NEUBERG and K. SCHWARZ (*Berlin. Klin. Woch.*, 1917, **54**, 84—87; from *Physiol. Abstr.*, 1918, **2**, 584).—The non-photosensitive substances of animal and plant tissue become photosensitive in the presence of certain inorganic salts, particularly those of iron. These salts act as photocatalysts, taking oxygen from the air and passing it on to the organic light receptors. Under these conditions, leuco-compounds and quinol pass into the quinonoid form, the change being reversible. Proteins are also affected. This photosensitivity is increased by the application of mineral waters containing heavy metals. W. G.

The Possible Origin of the Toxicity of Ultra-violet Light. F. L. HARRIS and H. S. HOYT (*Science*, 1917, **46**, 318—320; from *Physiol. Abstr.*, 1918, **2**, 656).—Paramecia were experimented

with. Ultra-violet rays are detoxicated by passage through solutions of gelatin peptone, aminobenzoic acid, cystine, tyrosine, and leucine, the protective action of tyrosine being exceptionally marked in alkaline solution. Solutions of other substances investigated had no appreciable effect. These results agree with the view that the susceptibility of protoplasm to ultra-violet light is conditioned by the selective absorption of the toxic rays by the aromatic amino-acid radicles of the protoplasm. W. G.

Proteins of Cow's Milk. THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*, 1918, **33**, 7—17).—After the caseinogen has been removed from skim milk by precipitation with dilute sulphuric acid, the remaining proteins are thrown out by saturation with ammonium sulphate, and subsequently separated by treatment with magnesium sulphate. Lactoglobulin is insoluble in saturated magnesium sulphate solution, and contains 2·2% of phosphorus. When it is digested with alcohol, a phosphatide appears to be split off, and the remaining coagulated lactoglobulin now contains only 0·24% of phosphorus. A similar cleavage of phosphatide from vitellin occurs when it is treated with alcohol, and the authors suggest that these so-called globulins are really lecithalbumins or mixtures of proteins. Lactalbumin is soluble in saturated magnesium sulphate solution, and is practically free from phosphorus.

Although traces of proteoses can always be isolated from cow's milk, it is uncertain whether these substances are present as such in the fresh milk or are formed from the proteins by the reagents employed for their isolation. The "nucleon" described by Siegfried (A., 1897, ii, 219) is shown by the authors to consist probably of a mixture of uncoagulable protein and a still unidentified organic substance which yields phosphoric acid on hydrolysis.

By extraction of precipitated caseinogen with alcohol, a new protein is obtained which resembles the gliadin of wheat in its solubility in 50 to 80% alcohol. [See also *J. Soc. Chem. Ind.*, 1918, March.] H. W. B.

The Excretion of Substances Foreign to the Organism in the Urine. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 75—79).—Attention is directed to the fact that in the case of foreign substances excreted as conjugated or otherwise altered derivatives, the surface tensions of the latter in aqueous solution are greater than that of those of the former. Examples: benzoic acid and hippuric acid, menthol and menthol glycuronate, phenol and phenolsulphonic acid, phenol, catechol, and quinol. S. B. S.

Citric Acid in Urine. S. AMBERG and W. B. MCCLURE (*Amer. J. Physiol.*, 1917, **44**, 453—462; from *Physiol. Abstr.*, 1918, **2**, 683).—Citric acid can be detected in human urine by Kunz's pentabromoacetone method, or by Salant and Wise's method, a modification of Denigès's reaction. Preliminary experiments

indicate that about 500 mg. of citric acid are voided daily in the urine. W. G.

Salicylates. IX. Question of Salicyluric Acid in Salicyl Urines. PAUL J. HANZLIK (*J. Pharm. Exper. Ther.*, 1917, **10**, 461—490).—The author has been unable to isolate any salicyluric acid from urines after administration of salicylic acid, although all the methods for its isolation which have been published have been employed. In each case, only impure salicylic acid containing no glycine has been obtained. It appears improbable, therefore, that salicylates are converted into salicyluric acid in the human or animal organism. H. W. B.

Acidosis. IX. Relationship between Alkali Retention and Alkali Reserve in Normal and Pathological Individuals. WALTER W. PALMER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **32**, 499—507. Compare A., 1917, i, 523).—In normal persons, the urine becomes more alkaline than the blood ($p_H=7·4$) when the carbon dioxide present as hydrogen carbonate in the plasma exceeds 71 ± 5 volumes per cent. In most pathological cases, the urine does not become more alkaline than the blood until a higher level of hydrogen carbonate has been reached than in normal individuals. If, therefore, the administration of sodium hydrogen carbonate to a patient is continued until the urine turns alkaline, unnecessarily large and perhaps injurious quantities of hydrogen carbonate may be given. The therapeutic use of sodium hydrogen carbonate should therefore be controlled by estimations of the hydrogen carbonate in the plasma.

The alkali retention test (feeding with sodium hydrogen carbonate until the urine shows an alkalinity of $p_H=7·4$) indicates a greater acidosis than actually exists. If a positive result is obtained, it should be confirmed by blood analysis before being accepted. H. W. B.

The Nitrogenous Extractives of Tumours. JACK CECIL DRUMMOND (*Biochem. J.*, 1917, **11**, 246—254).—Four kinds of tumours of human and avian origin were extracted with boiling water, and after treatment with basic lead acetate the extracts were investigated in respect of their nitrogenous constituents. In general, the purine fraction was largest; adenine was found in all cases, and guanine, xanthine, and hypoxanthine in some. Small quantities of histidine, carnosine, and (probably) arginine were isolated from the avian tumour (Rous chicken sarcoma). Tyrosine and creatinine were present in all, and leucine in most cases (compare A., 1916, i, 866). J. H. L.

Formation of Creatine. Effects on the Excretion of Creatine in the Bird produced by Paraformaldehyde and Hexamethylenetetramine given separately and combined with Arginine Carbonate and other Substances. WILLIAM HENRY THOMPSON (*Biochem. J.*, 1917, **11**, 307—318).—It is suggested that formaldehyde, which probably takes part in the pro-

duction of methylated compounds, such as betaine, in plants and in the muscles of invertebrates, is formed also in the muscle tissue of vertebrates, and is disposed of by combination with a guanidine nucleus to form creatine. The increased excretion of creatine following the administration of arginine to ducks with their food (A., 1917, i, 673) becomes greater if paraformaldehyde is administered at the same time, although the latter alone has no effect. Paraformaldehyde ingested together with glycine, sarcosine, or guanidine carbonate also increases the production of creatine. Very much larger increases (in some cases six to eight times the normal amount) are produced by subcutaneous injection of paraformaldehyde alone or with arginine. Hexamethylenetetramine produces similar effects. The mechanism of the formation of creatine from arginine and formaldehyde in vivo is represented as involving conversion of the arginine into glycocyamine (compare Baumann and Hines, A., 1917, i, 677), methylation of the amino-group of the latter by interaction with two molecules of formaldehyde (compare Werner, T., 1917, **111**, 844), and isomeric change of the product into creatine by migration of the methyl group. J. H. L.

Lacquer Poisoning. I. Toyama and T. Kayaba (*Hifukwa Hitsunyokikwa Zasshi*, 1916, **16**, No. 7, 7—10; from *Physiol. Abstr.*, 1918, **2**, 693).—Lacquer poisoning may be produced in susceptible individuals by passing near a lacquer-tree or through a store containing lacquered articles. The poisoning is probably not due to a volatile constituent. The chief constituent of lacquer is urushiol, the chief poison having the composition $C_{15}H_{27}\cdot C_6H_3(OH)_2$. Lacquer also contains a hydrated and a methylated urushiol which are toxic, and a dimethylated and a hydro-dimethylated urushiol which are non-toxic (compare Majima, A., 1908, i, 437; 1909, i, 402, 945; 1912, i, 883). W. G.

Surface Tension of Solutions of Alkaloids. L. Berczeller and M. Seiner (*Biochem. Zeitsch.*, 1917, **84**, 80—105).—Stalagmometric measurements of solutions of salts of alkaloids, with additions of varying amounts of alkali, carried out with the object of illustrating Traube's theory of the connexion between surface tensions of solutions and toxic action. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Enzymes concerned in the Decomposition of Dextrose and Mannitol by Bacillus coli communis. II. Experiments of Short Duration with an Emulsion of the Organisms. Egerton Charles Grey (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 75—92. Compare A., 1914, i, 1034).—An emulsion of *B. coli communis*

in saline solution containing an amount of bacteria which would weigh, when dry, 1 gram, is sufficient completely to ferment 40 grams of dextrose in forty-eight hours in the presence of calcium carbonate. The author describes an ingenious device to prevent the settling of the latter during the experiment. The calcium carbonate is sewn up in small sacks of cloth, in each of which is placed also a small cork, the weights being so adjusted that the sacks just sink to the bottom of the flask when they are first introduced. During the course of the fermentation, the acid disengaged penetrates the sacks, and they become swollen with gas and rise to the top of the solution. During this movement up and down, the calcium carbonate contained in the sacks becomes gradually liberated, so that the solution is always turbid with calcium carbonate without being mechanically agitated from without. At the end of the experiment, the products of fermentation, namely, alcohol, carbon dioxide, formic, acetic, lactic, and succinic acids, are estimated in the solution. The actual amount of any of the products obtained is dependent on the concentration of salt and the temperature of fermentation. By comparison of the various amounts produced in different experiments, it is found that succinic acid and acetic acid are complementary as regards the extent of their formation, and are therefore probably produced from a common parent substance. Acetic acid and alcohol and alcohol and succinic acid are similarly related to one another, so that it would appear that the three substances, alcohol, acetic acid, and succinic acid, are formed from a common intermediate substance by the action of the same enzyme. The formation of lactic acid appears to be quite independent of that of the other products of fermentation, and its production is therefore due to a separate enzyme. The addition of peptone to the culture medium containing dextrose leads to the production of a greater proportion of lactic acid and a lesser proportion of alcohol, acetic acid, and succinic acid.

The products of the bacterial decomposition of mannitol closely resemble in amount those obtained from dextrose, which is in harmony with the author's view that the fermentation of various carbohydrates and allied substances by bacteria is effected by a single set of enzymes the action of which is common to all such cases of fermentation. The first step in the degradation of a particular molecular structure may require a special enzyme to produce the common intermediate substance, but the subsequent changes are always similar, being due to the action of the standard series of bacterial enzymes. [See also *J. Soc. Chem. Ind.*, 1918, 103A.]

H. W. B.

Enzymes concerned in the Decomposition of Dextrose and Mannitol by Bacillus coli communis. III. Various Phases in the Decomposition of Dextrose by an Emulsion of the Organisms. Egerton Charles Grey (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 92—106. Compare preceding abstract).—By examining portions of a fermenting solution containing dextrose and bac-

teria at the end of twelve, twenty-four, forty-eight, and seventy-two hours respectively, it is found that during the first twelve-hour period the number of living bacteria diminishes very rapidly, whilst during the second period a still more rapid growth of bacteria sets in, so that at its close the number present greatly exceeds that at the commencement of the experiment. Corresponding with these changes, there is a cessation in the production of lactic acid in the first period, the chief products being carbon dioxide, alcohol, and acetic and succinic acids, whilst subsequently in the third period, when the number of bacteria is at a maximum, the production of lactic acid is so much accelerated that it forms 70% of the fermented sugar. The period of exalted bacterial growth is associated with the transformation of a large proportion of the dextrose into a complex carbohydrate, which only reduces Fehling's solution after hydrolysis. The extent of the synthesis during this period is quantitatively of the same order as the degradation which ensues in the following period. A synthesis of fat was also observed on one occasion in circumstances which could not be again realised.

Since the amount of sugar decomposed during the first period in which the rapid diminution in the number of living cells occurs is as great as during the third period, in which the number of living cells both at the start and at the finish is enormonsly greater, the author draws the conclusion that the fermentation is brought about, not by the cells as such, but by enzymes in the cells. This conclusion is confirmed by the fact that different conditions result in variations in the amounts of the products of fermentation due presumably to the varied influence of the altered conditions on the operation of the different enzymes present. [See also *J. Soc. Chem. Ind.*, 1918, 103A.] H. W. B.

Influence of Conditions of Bacterial Cleavage of Proteins on the Cleavage Products. TAKAOKI SASAKI (*J. Biol. Chem.*, 1917, **32**, 527—532).—When *l*-tyrosine is acted on by *Bacillus coli communis* or *B. proteus vulgaris*, the chief product obtained depends on the composition of the medium employed. In the presence of lactose *p*-hydroxyphenylethylamine is produced, whilst if the lactose is replaced by Hendersen's phosphate mixture, the same bacteria form *d*-*p*-hydroxyphenyllactic acid withont any trace of the amine. H. W. B.

Stereochemistry of the Bacterial Decomposition of Albumin. TAKAOKI SASAKI and ICHIRO OTSUKA (*J. Biol. Chem.*, 1917, **32**, 533—538).—When *B. proteus vulgaris* or *B. coli communis* acts on *d*-tyrosine, *d*-*p*-hydroxyphenyllactic acid is formed. If now *B. subtilis* is substituted for either of the above bacilli, the product is *l*-*p*-hydroxyphenyllactic acid. The author suggests that an intermediate substance, probably of a ketonic nature, is first formed, which is then completely converted into one or other of the two possible asymmetric products. H. W. B.

Biochemical Study of Proteus vulgaris, Hauser. Comparison of the Properties of a Pathogenic Race and of a Saprophytic Race. F. G. VALLE MIRANDA (*Compt. rend.*, 1918, **166**, 184—187).—A comparison by ponderal methods of the biochemical properties of a *Proteus* isolated in a case of acute infantile gastro-enteritis and of another found in putrefying meat. These have been compared with respect to their behaviour towards carbohydrates, glycerol, gelatin, amino-acids, and tryptophan, and the results indicate that, despite their different origin, the two *Proteus* examined constitute two races of *Proteus vulgaris*, and not two distinct species. W. G.

Biochemistry of Pathogenic Anærobes. II. The Acid Production of Bacillus Welchii (B. perfringens) and Bacillus sporogenes (Metchnikoff). CHARLES GEORGE LEWIS WOLF and STEPHEN VEITCH TELFER (*Biochem. J.*, 1917, **11**, 197—212).—Dyer's method (A., 1917, ii, 157) was applied to the investigation of the volatile acids formed by *B. perfringens* and *B. sporogenes*, under anærobic conditions, in milk and in peptone broth containing 2% of dextrose. It was found that for the identification of the constituents of an unknown mixture of volatile acids the method must be applied, not only to the original mixture, but also to certain distillation fractions or even to secondary fractions. By this means useful comparative data may be obtained in the investigation of a number of mixtures, especially if the curves plotted are compared with those corresponding with mixtures of known composition; but very tedious fractionation would be required to obtain quantitative results, or even to detect such an acid as propionic in presence of acetic and butyric acids. The colour tests recommended by Dyer cannot be depended on until the acids have been separated.

The results of the present investigation indicate that in milk *B. sporogenes* forms acetic, hutyric, valeric, and hexoic acids, probably in the approximate proportions 25 : 17 : 16 : 41, whilst *B. perfringens* forms only acetic and butyric acids in the proportions 2 : 3. In the dextrose–peptone broth both organisms produce only acetic and butyric acids, in the proportions 3 : 2. These figures are given with great reserve; considerable amounts of propionic acid may have been present in all cases without being detected. For both organisms in milk the volatile acids constituted 68—69% of the total acids produced (both expressed in terms of alkali); for *B. sporogenes* and *B. perfringens* in dextrose–peptone the corresponding values were 55% and 50% respectively. J. H. L.

Biochemistry of Pathogenic Anærobes. III. The Effect of Acids on the Growth of Bacillus Welchii (B. perfringens) and Bacillus sporogenes (Metchnikoff). CHARLES G. L. WOLF and JOHN EDMUND GUY HARRIS (*Biochem. J.*, 1917, **11**, 213—245).—After an investigation of the effect of addition of different quantities of various acids on the reaction of peptone broth containing 2% of dextrose, the authors studied the influence of the initial reaction

of the medium, adjusted to various values between $p_H=6·5$ and $4·5$ by addition of acid, on the anærobic fermentation of *B. perfringens* and *B. sporogenes*. The acids employed were hydrochloric, formic, acetic, butyric, lactic, malic, and succinic. The main conclusions drawn may be summarised as follows.

The higher the initial hydrion concentration in the medium, the longer is the latent period of growth, *i.e.*, the time elapsing between inoculation and the first visible signs of growth; and if the initial hydrion concentration exceeds a certain critical value (about $p_H=4·8$ for *B. perfringens* and $p_H=4·9$ for *B. sporogenes*) no fermentation occurs. Where fermentation takes place, the final reaction attained is not a "physiological constant," but varies within comparatively narrow limits ($p_H=4·2—4·8$ for *B. perfringens* and $p_H=4·9—5·5$ for *B. sporogenes*), according to the initial reaction of the medium. Moreover, the form of the curve representing the dependence of final on initial reactions, designated the "reaction resultant," is to a certain extent characteristic of the particular acid to which the initial reaction is due. The change in the value of p_H during fermentation is not a measure of the amount of acids produced. In the case of *B. perfringens*, the production of acids and carbon dioxide is practically independent of the initial reaction when the latter is due to hydrochloric acid. With feebly dissociated acids, on the other hand, much larger amounts are required to produce the same initial hydrion concentrations, and these acids appear to exert an inhibitive influence on fermentation apart from that due to their cations. *B. sporogenes* differs from *B. perfringens* in that, in media of which the initial reaction is near the critical point, the final reaction may be less acid than the initial. This is attributed to the production of large amounts of basic and amphoteric substances which reduce the acidity and act as buffers. Cessation of growth is probably due almost entirely to accumulation of metabolites.

It is suggested that by treatment of gas gangrene infections by means of highly buffered solutions with hydrion concentrations slightly above the critical value, growth might be inhibited.

J. H. L.

Ptomaines and War Wounds. ALBERT BERTHELOT (*Compt. rend.*, 1918, **166**, 187—189).—The author has endeavoured to show that toxic ptomaines may be formed by the action, on the blood, of proteolytic and amino-acid splitting microbes likely to be found in wounds, and considers that his experimental results support this idea.

W. G.

The Autolysis of Yeast and the Influence of its Products of Proteolysis on the Development of Yeast and of Lactic Bacteria. PAUL VANSTEENBERGE (*Ann. Inst. Pasteur*, 1917, **31**, 601—630).—After death the yeast-cell loses its cell water and diminishes in size. If the enzymes present have not been destroyed after a time varying with the temperature, liquefaction of the yeast occurs. For the endotryptase the optimum temperature is

45—50° and the maximum temperature 53°. For autolysis yeast in the living state the optimum temperature is 48—50°. progress and completion of the autolysis are best shown by increase in the acidity to a certain maximum and the separat of tyrosine in a crystalline state from the autolysate. When ye is boiled with water, the extract only contains one-third of total nitrogen, but if the boiling is preceded by an autolysis 48° lasting twenty-three hours, the whole of the nitrogen is obtai in a form soluble in water and not coagulated by heat. An extr of autolysed yeast is much more nutritive for yeast and for la bacteria than an extract of fresh yeast, and the nitrogen is c verted by the autolysis into a form more readily assimilable by th organisms.

In an extract of autolysed yeast of a strength equivalent 20 grams of yeast per 100 c.c., there are certain products unfavo able to the development of yeast, but this injurious action dis pears on dilution. Such products are tyrosine and leucine, of wh the former is injurious at concentrations over 0·05% and the lat at concentrations above 0·08%. At the concentrations at wh these substances are present in autolysed yeast they inhibit development of yeast, but do not exert any unfavourable influe on lactic bacteria. [See also *J. Soc. Chem. Ind.*, 1918, 103A.]

W. G

The Action of Arsenic Salts on Yeast. F. Boas (*Zeits Gärungsphysiol.*, 1917, **6**, 1—12; from *Physiol. Abstr.*, 1918, 631).—Sodium metarsenite retards fermentation by living yea Fermentation is at first arrested by alkali arsenates, but, in presence of soluble nitrogen, it is promoted after five to se hours. Although in nitrogen-free solutions the inhibiting act is very strong, yet in some cases after twenty-four hours fermen tion had proceeded under these conditions. Owing to differ physiological conditions of the yeast, considerable variation in results was noticeable.

W. G

The Water-soluble Accessory Growth-promoting S stance in Yeast. Jack Cecil Drummond (*Biochem. J.*, 1917, 255—271).—The opinion of McCollum and Kennedy (A., 19 i, 461), that the "water-soluble growth-promoting factor B" identical with the antineuritic vitamine, is confirmed, inasmuch it is now shown, by feediug experiments with rats, that the wa soluble factor in yeast possesses many of the properties of the an neuritic principle, such as insolubility in ether or absolute alco and relative insensitiveness towards heat, dilute acids, alkalis. Unsuccessful attempts to isolate the active substance fr yeast are described. The water-soluble factor is not identical w adenine, nucleic acid, or any of the constituents of commer meat extract. [See also *J. Soc. Chem. Ind.*, 1918, 134A.]

J. H. I

Intermediary Reactions in Alcoholic Fermentation. H. EULER, HJ. OHLSEN, and D. JOHANSSON (*Biochem. Zeitsch.*, 1917, **84**, 402—406).—A Swedish beer-yeast was dried at 40°, and extracted with water. Such an extract contains a phosphatase, which acts directly on lævulose. Dextrose is not, however, acted on by it unless previously treated with fresh yeast. A Swedish yeast, weakened by being kept for six weeks in a solution containing sodium chloride, sugar, but no nitrogen, could esterify lævulose but not dextrose. The results confirm Harden's view (compare A., 1908, i, 590) that the hexose phosphate is a derivative either of lævulose or of a closely allied sugar, and that the dextrose must be converted into this in order to form the phosphate ester.

S. B. S.

Is Lactic Acid an Intermediate Product of Alcoholic Fermentation? ALEXANDRE LEBEDEV (*Biochem. J.*, 1917, **11**, 189—196).—The balance of experimental evidence is considered to be unfavourable to the view that lactic acid is an intermediate product of fermentation. The conclusions of Palladin and Sabinin on this subject (A., 1916, i, 620) are criticised. In the decomposition of lactic acid by yeast-reductase in presence of methylene-blue the quantity of acetaldehyde formed is much smaller than corresponds with the equation given (*loc. cit.*), and when pyruvic acid is substituted for methylene-blue very little alcohol is formed in comparison with the amount of carbon dioxide. Pyruvaldehyde is a more probable intermediate product of fermentation than lactic acid, for at very low concentrations it is decomposed by yeast into practically equivalent amounts of alcohol and carbon dioxide, but, on the other hand, it is fermented only very slowly and is toxic towards yeast enzymes. The evidence regarding the possible formation of pyruvic acid in the course of alcoholic fermentation is inconclusive. J. H. L.

Influence of Metallic Salts on Germination in the Presence of Calcium. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1918, **166**, 89—92).—A continuation of previous work (compare A., 1917, i, 530), the peas being germinated in water containing the various salts examined, either with or without the addition of calcium in the form of its sulphate or chloride. The root measurements show that the presence of any salt, in amount approaching the toxic quantity in pure water, lessens or prevents the favourable action exerted by calcium when present alone. Thus the different metals, whether toxic or alimentary, function as antagonists to calcium in germination, in the same way as calcium behaves as an anti-toxic towards them. The physiological action of a mixture is thus not equal to the sum of the actions of its constituents.

W. G.

Action of Acids on Plants. I. ONODERA (*Ber. Ohara Inst. Landw. Forsch.*, 1916, **1**, 53—100; from *Physiol. Abstr.*, 1918, **2**,

707).—In general, plant growth was considerably stimulated by moderately concentrated acids, and in particular by nitric acid in the form of carbamide nitrate containing 0·05 gram per litre. The acids investigated, arranged in descending order of toxicity, were: hydrochloric, sulphuric, formic, butyric, acetic, nitric, and α-hydroxypropionic. Plants grown in an acid culture develop abnormally in height, their root development being quickly arrested, but the growth of the foliage is continuous. W. G.

The Effect of certain Organic Compounds on Plant Growth. M. J. FUNCHESS (*Alabama Agric. Expt. Stat. Bull.*, 1916, **191**, 103—132; from *Physiol. Abstr.*, 1918, **2**, 707—708).—Pot experiments were conducted to determine the effect of coumarin, vanillin, pyridine, quinoline, dihydroxystearic acid, and pyrogallol on plant growth in the case of oats and wheat grown on red clay or a sandy soil. Pyridine and quinoline were found to be beneficial in the soils used. The compounds used in small amounts were not found to be harmful to growth. Vanillin applied at the rate of 5—10 parts per 10,000 was quite harmful to oats grown on the sandy soil, in the presence or absence of complete fertilisers, but there was no residual harmful effect. Similar results were obtained with coumarin. The conclusion is drawn that rapid chemical or biochemical transformation of these compounds into inert forms occurs in unsterilised soils under the above experimental conditions, and that the results obtained with soil cultures do not agree with those obtained with solution cultures. W. G.

Action of Various Fertilisers, especially Manganese Sulphate, on the Growth of Oats. L. HILTNER and G. KORFF (*Prakt. Blätt. Pflanzenbau & Pflanzenschutz*, 1917, **15**, 549—556; from *Bied. Zentr.*, 1918, **47**, 15—19).—The authors describe pot experiments in which oats were grown in various types of soils, some of which were treated with iron, copper, or manganese sulphates, or with sulphur, and all received guano. The addition of manganese sulphate caused in each case an increase in the size of the plant and in the total number of oat-grains, especially in soils containing much humus. In peaty soils, the yield of oat-grains was seventy times as great in the presence of manganese sulphate as in its absence. It is suggested that these remarkable results are largely due to the accelerating action of manganese on the oxidation of the guano added to the soil. The other sulphates and the sulphur experimented with produced similar, but not such marked results. [See also *J. Soc. Chem. Ind.*, 1918, March.]
H. W. B.

The Necessity for an Acceptor of Hydrogen and an Acceptor of Oxygen for the Manifestation of the Processes of Oxido-reduction in Organic Liquids of Animal and Vegetable Origin. J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1918, **166**, 130—132).—It has been shown by Bach (compare A., 1917, i, 375, 431) that the presence of a readily oxidisable sub-

stance is necessary for the reduction of alkali nitrates by milk or potato juice, and the authors now show that the presence of a readily reducible substance is essential for oxidation under similar conditions.

W. G.

The Relationship between the Osmotic Concentration of Leaf Sap and Height of Leaf Insertion in Trees. J. ARTHUR HARRIS, ROSS AIKEN GORTNER, and JOHN V. LAWRENCE (*Bull. Torrey Bot. Club*, 1917, **44**, 267—286 [reprint]).—Measurements have been made on leaves gathered from different heights on twenty-six trees belonging to twelve species. The results indicate that the osmotic concentration of the leaf sap, as determined by the freezing-point lowering method, increases from lower to higher levels. The specific electrical conductivity, K, shows a tendency to decrease from lower to higher levels, but the results obtained are not very regular. The ratio K/Δ, where Δ is the lowering of the freezing point, however, shows a regular decrease from lower to higher levels. The authors have endeavoured to establish a formula showing the relationship between the increase in osmotic concentration and the difference in heights of insertion of the leaves plus the resistance to the passage of water moving at the rate of the transpiration stream opposed by conducting tracts equal in length to the differences in the heights of insertion. The value for the latter factor is, however, not yet definitely established.

W. G.

Genesis of Inulin in Plants. H. COLIN (*Compt. rend.*, 1918, **166**, 224—227).—Estimations of the total sugar, reducing sugar, sucrose, starch, and inulin in the various organs of the plant in the case of chicory, dahlias, and Jerusalem artichokes show that there can be no question of the immediate elaboration of inulin by the leaf and of its migration, as such, to the subterranean organs. The leaves only deliver to the plant the sugars the condensation of which takes place in the stem or only in the tubercles or the roots.

W. G.

The Constituents of Wood which give Colour Reactions. II. H. WICHELHAUS and MARTIN LANGE (*Ber.*, 1917, **50**, 1683—1685. Compare A., 1916, i, 874).—About 98 litres of distillate have been collected from 1200 grams of pine or fir wood by the passage of a current of steam at 180—200°, and separated by a second distillation into two fractions. The first two-thirds gave a green precipitate with phloroglucinol and hydrochloric acid, whilst the last third gave the typical cherry-red precipitate, and also formed a brick-red *substance*, $C_{18}H_{18}O_7N_6$, with *p*-nitrophenylhydrazine. The latter is apparently a condensation product of a ketofurfuraldehyde, $C_6H_6O_3$, derived from a hexose as follows: $C_6H_{12}O_6 - H_2O + O = C_6H_6O_3 + H_2O$. [See also *J. Soc. Chem. Ind.*, 1918, March.]

J. C. W.

The Constituents of the Bark of the Hymenodyctyon excelsum. CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN

(*J. Proc. Asiatic Soc., Bengal*, 1916, [N.S.], **12**, 161 [reprint]).—The authors have confirmed Broughton's work (1870) in that they were able to isolate æsculin and scopoletin from the bark of the *Hymenodyctyon excelsum*, but they were unable to find any traces of an alkaloid (compare Naylor, A., 1883, 1141; 1885, 565).

W. G.

The Loganberry and the Acid Content of its Juice. MILO REASON DAUGHTERS (*J. Ind. Eng. Chem.*, 1918, **10**, 30).—Analyses are given of the loganberry and of its juice. The chief acid in the fruit is citric; tartaric and volatile acids are present in traces; malic acid is absent. [See also *J. Soc. Chem. Ind.*, 1918, March.]

L. A. C.

Soil Acidity and the Hydrolytic Ratio in Soils. C. H. SPURWAY (*J. Agric. Research*, 1917, **11**, 659—672).—The examination of a number of soils from glacial formations indicates that the reaction of these soils is probably determined chiefly by the hydrolytic ratio between salts of the alkaline earth metals on the one hand and those of iron and aluminium on the other, when these are in equilibrium; the hydrolytic ratio depending on the concentration and degree of hydrolysis of each salt in the presence of the other when equilibrium is reached. [See also *J. Soc. Chem. Ind.*, 1918, 132A.]

W. G.

Isolation of *p*-Hydroxybenzoic Acid from Soil. E. H. WALTERS (*J. Amer. Chem. Soc.*, 1917, **39**, 1778—1784).—*p*-Hydroxybenzoic acid and benzoic acid have been isolated from a soil in the orange groves of Florida. The soil is largely composed of quartz sand mixed with organic matter, which can be almost entirely removed by washing with dilute sodium hydroxide. The actual quantities of the pure acids obtained correspond with about 21·6 parts of *p*-hydroxybenzoic acid and 1·7 parts of benzoic acid per million.

J. C. W.

Alkali Soils: Biochemical Factors in their Reclamation. J. H. BARNES and B. ALI (*Agric. J. India*, 1917, **12**, 368—380; from *Physiol. Abstr.*, 1918, **2**, 712).—Ordinary alkali land contains all the organic life associated with soil fertility, but in a more or less dormant state. In the more saline soils of long duration the vitality of these organisms is somewhat impaired. Nitrifying organisms are thus dormant in alkali soils so long as the saline matter is in excess, but washing of such soils is followed by increased nitrification, and this will commence before the soil is sufficiently washed to admit of the growth of crops, as nitrifying organisms can exist in a solution of higher osmotic pressure than can the higher plants. Ammonifying organisms are still more hardy than the nitrifying organisms to saline matter. There is an indication that the activity of nitrogen-fixing bacteria of the *Azotobacter* type is increased after washing.

W. G.

Organic Chemistry.

Solubility of Lead Acetate in Water. Yukichi Osaka and Reijiro Hara (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 147—150).—Measurements have been made of the solubility of lead acetate in 0·025, 0·05, and 0·1*N*-acetic acid at 25°, 35°, and 45°. The quantity of salt dissolved per 100 grams of water increases slightly with the acidity of the solution, the relation being linear. By extrapolation, the solubility in pure water is found to be 54·38 parts per 100 of water at 25°, 87·77 at 35°, and 154·25 at 45°. These extrapolated values are based on the assumption that the salt is not hydrolysed. H. M. D.

Physical Properties of a Number of Pure Esters. J. Howard Matthews and Katharine E. Faville (*J. Physical Chem.*, 1918, **22**, 1—21).—The esters, obtained from Kahlbaum, were purified by chemical treatment according to the method described by Young and Thomas (T., 1893, **63**, 1191), and then subjected to fractional distillation in an apparatus devised to give a constant pressure of 760 mm. In accordance with the results obtained by most of the previous observers, the boiling points of the esters were found to extend over an appreciable range. The physical properties measured were the boiling point, density, viscosity, specific inductive capacity, and refractive index, the values being recorded in the table.

	B. p.	D_4^{20}.	$\eta_{20°}$.	$\epsilon_{20°}$.	n_D.
*iso*Amyl formate ...	123·46°—123·56°	0·8773	0·789	4·98	1·39772
*iso*Butyl formate ...	98·15 — 98·25	0·8832	0·638	5·93	1·38568
Propyl acetate ...	101·57 —101·77	0·8869	0·585	8·10	1·38422
Ethyl propionate ...	99·12 — 99·22	0·8904	0·545	5·75	1·38414
Propyl propionate ...	121·0 —121·25	0·8809	0·674	4·66	1·39325
Ethyl butyrate ...	120·0 —120·5	0·8784	0·665	5·91	1·40002
*iso*Butyl valerate ...	167·0 —168·5	0·8544	1·118	8·21	1·40569

The boiling points of the esters at various pressures were also determined, and the results applied in testing the deductions made by van der Waals in reference to the theory of corresponding states. For ethyl propionate, ethyl butyrate, and *iso*butyl formate, critical data have been previously determined, and by making use of these a comparison is made of the values of the ratios of the absolute temperatures at corresponding pressures to the absolute critical temperatures. For a given pressure, the temperature ratio varies appreciably with the nature of the ester, but the deviations from constancy are less than those found by Young and Thomas in their investigation of a series of ten esters. H. M. D.

Relation between the Affinity Values of the Aliphatic Acids of the Mono- and Di-basic Series. Gervais le Bas (*Chem. News*, 1918, **117**, 121—122).—Tables of the affinity values ($k \times 10^4$)

of monobasic fatty acids, starting with formic acid, and of dibasic fatty acids, starting with succinic acid, are given. The latter form a nearly arithmetical series, that is, the values for $n(k \times 10^4)$, where n represents the position in the series, are very nearly the same. If the numbers for the members of the dicarboxylic acid series be divided by the numbers for the members of the monocarboxylic acid series, a series of numbers is obtained which, when plotted against successive integers, gives a curve resembling a rectangular hyperbola. The free energy due to the carboxylic group in the monobasic acid series diminishes with the increase in the length of the hydrocarbon chain. When two such groups are present in the same molecule the ratio between the affinity values varies inversely with the number of carbon atoms between the groups, except in the case of oxalic and succinic acids, the ratio of which shows a greater increase. In the dicarboxylic acid series the two carboxylic groups are mutually active, the one increasing the tendency of the other to be active or possess residual affinity, but the latter function varies inversely with the number of interposed methylene groups. The following formula for the dicarboxylic acids, in which these facts have been noted, is suggested:

$$CH_2 < \begin{matrix} CH_2—CH_2—CO_2H \\ CH_2—CH_2—CO_2H \end{matrix}$$

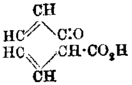
C. A. M.

Method of Preparing Acetaldehyde. UNION CARBIDE Co. (U.S.-P., 1247270, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 74A).—Acetylene is combined with the elements of water in an acid bath containing a mercury compound. The bath is maintained at such a temperature that the acetaldehyde distils continuously, and the mixture of acetaldehyde and acetylene is conducted into a series of baths similar to the first bath. W. P. S.

The Wagner-Saytzeff Reaction with Mesityl Oxide. C. J. ENKLAAR (*Chem. Weekblad*, 1918, **15**, 188—190).—The liquid obtained by the action of zinc, mesityl oxide, and allyl bromide, in presence of anhydrous ether, yields on distillation two fractions, in addition to unchanged products. The first fraction has b. p. 71°/20 mm., and consists of βδ-dimethyl-$\Delta^{\alpha\epsilon}$-heptadien-δ-ol mixed with a smaller proportion of a ketone, $C_9H_{16}O$, probably a dimethylheptenone.

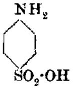
The second fraction has b. p. 140—142°/3 mm., and its constituents have not been identified. A. J. W.

Influence of different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. III. Constitutional Formulæ of the Hydroxybenzoic Acids and of Sulphanilic Acid. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 581—589. Compare A., 1917, i, 631; this vol., i, 101).—Salicylic acid behaves in alkaline solution as a monobasic acid in

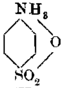


retarding the destruction of dextrose, whereas *m*- and *p*-hydroxybenzoic acids behave as dibasic acids. The author considers that these results support the constitutional formula (annexed) assigned to salicylic acid by Brunner (compare Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910).

Sulphanilic and hippuric acids behave as monobasic acids in alkaline solutions, and are neutral in their influence on the inversion of sucrose by hydrochloric acid. On these grounds the author assigns the constitution I to sulphanilic acid in alkaline solution and constitution II in acid solution.



(I.)



(II.)

[See also *Ind.*, 189A.*] W. G.

Lactose. II. A. Smits and J. Gillis (*Proc. K. Akad. Wetensch Amsterdam*, 1918, **20**, 573—580. Compare this vol., i, 101).—From a study of the results previously given (*loc. cit.*), coupled with those obtained by Hudson (compare A., 1909, ii, 131; 1910, i, 220), the authors consider that mutarotation is not due to a slow dehydration process in the sugar series, as was assumed by Hudson, but to the slow establishment of an internal equilibrium between two stereo-isomeric forms. Further, that for the unsubstituted aldoses, such as dextrose, galactose, lactose, etc., the presence of water of hydration does not change anything in the structure of the asymmetric terminal carbon atom. The pseudo-ternary $T-x$ figure of the system water–α-lactose–β-lactose is given, and the surface of equilibrium lying in it is shown. W. G.

The Reduction of the Group $\cdot CH_2I$ attached to Nitrogen. Amand Valeur and Emile Luce (*Compt. rend.*, 1918, **166**, 392—394. Compare this vol., i, 102).—Dimethyliodomethyl-δ-iodoamylammonium iodide, $CHMeI\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_2I\cdot CH_2I$, when reduced by zinc in alcohol or in dilute acetic acid, gave trimethylamylammonium iodide, $CH_2Me\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_3I$, together with a small amount of an unsaturated methiodide. Methylene-desdimethylpiperidine iodide when similarly reduced gave des-dimethylpiperidine methiodide [trimethyl-Δ^{δ}-pentenylammonium iodide], m. p. 227—229°, giving an aurichloride, m. p. 107°. Dimethyliodomethyl-Δ^{γ}-pentenylammonium iodide,

$$CHMe:CH\cdot CH_2\cdot CH_2\cdot NMe_2I\cdot CH_2I,$$

when reduced gave a mixture of two isomeric unsaturated *methiodides*, $C_8H_{18}NI$, giving two *aurichlorides*, having m. p.'s 116° (decomp.) and 89—91° respectively. Trimethyliodomethylammon-

* In cross references to abstracts, *Ind.* will be used in place of *J. Soc. Chem. Ind.*, 1918, **37**.

ium iodide when reduced by zinc and acetic acid yielded tetramethylammonium iodide. W. G.

Isethionic Acid Derivatives of some Aliphatic Amino-acids. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1917, **101**, 1—14. Compare A., 1916, i, 815).—A mixture of equimolecular quantities of the amino-acid and isethionic acid is dissolved in water, heated on the water-bath, and finally at 140—143° for three and a-half to four hours. The cooled mass is dissolved in water, and the product of the reaction precipitated by alcohol. It is then recrystallised from dilute alcohol with the aid of animal charcoal. *Isethionylglycine*, $CO_2H\cdot CH_2\cdot NH\cdot SO_2\cdot C_2H_4\cdot OH$, does not melt below 260°; it gives a crystalline *copper* salt. *Isethionylalanine*, $C_5H_{11}O_5NS$, has m. p. 242° (decomp.), and *isethionylleucine*, $C_8H_{17}O_5NS$, m. p. 260° (decomp.). The three compounds have several properties in common; the aqueous solution is acid to litmus, but neutral to Congo-red, unless the solution is very concentrated. Phosphotungstic acid does not produce a precipitate, but only a turbidity, which disappears on warming and reappears on cooling. They reduce ammoniacal silver nitrate and when heated give off sulphur dioxide and a gas, of which the odour resembles that of mercaptan.

A similar compound appears to be formed between isethionic acid and aspartic acid, but it could not be isolated in a crystalline condition. H. W. B.

Action of Formaldehyde on Glycine and its Metallic Salts. HUGO KRAUSE (*Ber.*, 1918, **51**, 136—150).—The use of formaldehyde in the titration of glycine is now a matter of common knowledge, but no definite work has yet appeared on the nature of the reaction between these compounds, or on the behaviour of the metallic salts of glycine. It is now shown that the salts react like the free amino-acid, and that the products, which may be isolated, in all cases correspond with a condensation product of the formula $C_7H_{14}O_5N_2$. Allowing $C_4H_8O_4N_2$ for two glycine residues, it follows that this product can only be written as

$$OH\cdot CH(CH_2\cdot NH\cdot CH_2\cdot CO_2H)_2.$$

From a measurement of the amount of formaldehyde which takes part in the reaction, the very puzzling discovery is made that only one molecule of the aldehyde is required for one of the acid. This is explained by the fact that the methyl alcohol present in the formalin used also enters into the process. If pure formaldehyde solution is used, very little of the compound is formed, relatively much more formaldehyde disappears, and a considerable amount of formic acid is produced. It can be proved, moreover, by a rough quantitative method, that methyl alcohol disappears. The normal reaction is therefore expressed in the equation $2NH_2\cdot CH_2\cdot CO_2H + 2CH_2O + CH_3\cdot OH = C_7H_{14}O_5N_2 + 2H_2O$, whilst the pure aldehyde reacts according to the equation $2NH_2\cdot CH_2\cdot CO_2H + 4CH_2O = C_7H_{14}O_5N_2 + H\cdot CO_2H + H_2O$.

The existence of the $-CH\cdot OH$ group in the molecule is proved by the facts that methyl and ethyl alcohols are formed on heating

the product, that the compound yields an acetate, and that acetone is formed, in traces, by oxidation with chromic acid.

A full account of the isolation of the products is given, and also of the application of the barium salt to the settlement of the above questions. Free *β-hydroxytrimethylenediglycine* is a deliquescent white powder, which decomposes at above 75°, restores the colour of Schiff's reagent, and decomposes alkali carbonates with vigorous effervescence, and its *acetate* is also white. The *sodium* salt, $1H_2O$, and *calcium* salt, $2H_2O$, are deliquescent powders with alkaline reactions; the *barium* salt, $3H_2O$, crystallises in flat rods or leaflets, is not hygroscopic, and is only soluble in 22 parts of water at 18°; the *magnesium* salt, $3H_2O$, and an acid *salt*,

$$C_7H_{12}O_5N_2Mg,0{\cdot}25C_7H_{14}O_5N_2,2{\cdot}5H_2O,$$

are somewhat hygroscopic; copper glycine gives a fairly insoluble deep blue *salt* of the formula $C_7H_{12}O_5N_2Cu,3H{\cdot}CHO$; with silver glycine, a white precipitate, probably of the normal salt, is formed momentarily, but this soon changes into a yellow *salt*, according to the equation, $C_7H_{12}O_5N_2Ag_2 + 2H_2O = 2OH{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Ag + CH_3{\cdot}OH$. J. C. W.

Action of Ethyl Oxalate on Ethyl β-Aminocrotonate. WILHELM WISLICENUS and KARL SCHÖLLKOPF (*J. pr. Chem.*, 1917, [ii], **96**, 174—179).—The interaction of ethyl oxalate and ethyl β-aminocrotonate in the presence of alcoholic-ethereal potassium ethoxide follows the course stated by Benary, Reiter, and Svenderop (A., 1917, i, 252), the product being the yellow potassium derivative, $CO_2Et{\cdot}C(OK){:}N{\cdot}CMe{:}CH{\cdot}CO_2Et$, of ethyl *N*-ethoxalylaminocrotonate, from which the free ester is liberated on acidifying. In the presence of water, the potassium derivative readily undergoes partial hydrolysis with formation of ethyl β-oxalylaminocrotonate, prisms, which after dehydration have m. p. 106—108°. If ethyl aminocrotonate is allowed to react with a bimolecular proportion of ethyl oxalate and of potassium, a deep yellow dipotassium compound, $C_{12}H_{11}O_7NK_2$, is obtained, probably a cyclic derivative of ethyl *N-C*-diethoxalyl-β-aminocrotonate; on treatment with dilute mineral acid, the aqueous solution of this dipotassium compound deposits yellow needles of a *compound*, $C_{12}H_{12}O_7NK$, containing only one atom of potassium. D. F. T.

The Nitrogenous Pigments of Molasses. H. FRIEDRICH (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 769—771). VL. STANĚK (*ibid.*, 771—773).—Polemical. Friedrich's reply to Staněk's criticism (A., 1917, i, 545), and a rejoinder. J. C. W.

The Pseudo-system Methyl Thiocyanate, Methylthiocarbimide and Trimethyl Trithiocyanate. J. GILLIS (*Chem. Weekblad*, 1917, **15**, 48—78).—An investigation of the curves of solidification and ebullition of mixtures of methyl thiocyanate and methylthiocarbimide. A. J. W.

Organo-Cadmium Compounds. I. Simple Cadmium Alkyls. ERICH KRAUSE (*Ber.*, 1917, **50**, 1813—1822).—Cadmium dialkyls can be readily obtained by adding finely powdered, dry

cadmium bromide to ethereal solutions of the magnesium alkyl bromides and distilling the product in a high vacuum. The pure compounds are colourless, highly refractive oils with very unpleasant odours and irritating action on the mucous membrane. The lower members are remarkably volatile, especially in ether vapour, and it is also interesting that the boiling points range higher than those of the corresponding mercury dialkyls. The oils are permanent if stored in tubes filled with pure nitrogen in the dark, but with traces of air and moisture they soon become steely-blue, especially in the light. Cadmium dimethyl merely gets coated with a white crust of the methoxide on exposure to the air, but the others are vigorously oxidised, and even inflame if allowed to fall in drops. The oils sink in water, and then if shaken begin to decompose with a crackling noise, which proceeds for hours. They are mostly stable, in an indifferent atmosphere, up to about 180°, when they decompose so vigorously that part of the liberated metal melts to brilliant drops and another part is deposited as a mirror.

The atomic refraction and dispersion of cadmium in these alkyls rise steadily with the molecular weights, but, taking averages, they are remarkably high compared with the constants for mercury and zinc.

Cadmium dimethyl has m. p. −4·5°, b. p. 105·5°/758 mm., $D_4^{17·9}$ 1·9846, n_{H_α} 1·57766, n_D 1·58488, n_{H_β} 1·60381, n_{H_γ} 1·62053, at 17·9°. *Cadmium diethyl* has m. p. −21°, b. p. 64°/19·5 mm., $D_4^{18·1}$ 1·6564, n_{H_α} 1·56512, n_D 1·56798, n_{H_β} 1·58447, n_{H_γ} 1·59887, at 18·1°. *Cadmium di-n-propyl* has m. p. −83°, b. p. 84°/21·5 mm., $D_4^{17·6}$ 1·4201, n_{H_α} 1·52412, n_D 1·52906, n_{H_β} 1·54267, n_{H_γ} 1·55452, at 17·6°. *Cadmium di-n-butyl* has m. p. −48°, b. p. 103·5°/12·5 mm., $D_4^{19·5}$ 1·3056, n_{H_α} 1·51100, n_D 1·51546, n_{H_β} 1·52762, n_{H_γ} 1·53793, at 19·5°. *Cadmium diisobutyl* has m. p. −37°, b. p. 90·5°/20 mm., D_4^{18} 1·2693, n_{H_α} 1·49528, n_D 1·49966, n_{H_β} 1·51160, n_{H_γ} 1·52173, at 18°. *Cadmium diisoamyl* has m. p. −115°, b. p. 121·5°/15 mm., D_4^{19} 1·2210, n_{H_α} 1·49967, n_D 1·50389, n_{H_β} 1·51470, n_{H_γ} 1·52412, at 19°.

All densities are reduced to vacuum standard. J. C. W.

Some mixed Tin Tetra-alkyls and Tin Trialkyl Haloids. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, **50**, 1802—1807).—The physical constants of some twenty known organo-tin compounds are tabulated, and an account is given of about twenty new compounds of the same nature. The material is being gathered for an investigation on the atomic refraction of tin and for studies on compounds containing tin chains (compare following abstract).

Mixed tin tetra-alkyls are prepared by heating tin trialkyl bromides with three times the theoretical quantity of magnesium alkyl haloids, first in ether and then at 100°, and they are converted into the tin trialkyl bromides by the action of bromine at −40° to −30°, the rule being that the lightest alkyl group is displaced (compare lead; A., 1917, i, 256). The chlorides are made from the bromides by shaking their ethereal solutions with [illegible]

sodium hydroxide (or silver hydroxide in the case of the methyl compounds), and then adding hydrochloric acid to the ethereal extract of the tin trialkyl hydroxide.

Tin triethylisobutyl has b. p. 96·5°/17 mm., $D_4^{20\cdot3}$ 1·1390, n_{H_α} 1·46977, n_D 1·47304, n_{H_β} 1·48132, n_{H_γ} 1·48826, at 20·3°. *Tin dimethyldiisobutyl* has b. p. 85°/16·5 mm., $D_4^{20\cdot1}$ 1·1179, n_{H_α} 1·46037, n_D 1·46354, n_{H_β} 1·47165, n_{H_γ} 1·47851, at 20·1°. *Tin triethylisoamyl* has b. p. 111°/18·5 mm., $D_4^{20\cdot1}$ 1·1203, n_{H_α} 1·46917, n_D 1·47243, n_{H_β} 1·48050, n_{H_γ} 1·48739, at 20·1°. *Tin ethyltri-*n*-propyl* has b. p. 117·5/23·5 mm., $D_4^{21\cdot8}$ 1·1225, n_{H_α} 1·47053, n_D 1·47374, n_{H_β} 1·48197, n_{H_γ} 1·48890, at 21·8°. *Tin diethyldiisobutyl* has b. p. 108·2°/13 mm., $D_4^{20\cdot4}$ 1·1030, n_{H_α} 1·47036, n_D 1·47361, n_{H_β} 1·48167, n_{H_γ} 1·48846, at 20·4°. *Tin tri-*n*-propylisobutyl* has b. p. 128°/18 mm., $D_4^{24\cdot1}$ 1·0841, n_{H_α} 1·46929, n_D 1·47245, n_{H_β} 1·48042, n_{H_γ} 1·48711, at 24·1°. *Tin diethyldiisoamyl* has b. p. 131°/13·5 mm., D_4^{19} 1·0725, n_{H_α} 1·46957, n_D 1·47268, n_{H_β} 1·48040, n_{H_γ} 1·48694, at 19°. *Tin ethyltriisobutyl* has b. p. 125°/16 mm., D_4^{21} 1·0779, n_{H_α} 1·47053, n_D 1·47371, n_{H_β} 1·48167, n_{H_γ} 1·48830, at 21°. *Tin ethyl-*n*-propyldiisoamyl* has b. p. 141—142°/17 mm., $D_4^{21\cdot9}$ 1·0654, n_{H_α} 1·46902, n_D 1·47214, n_{H_β} 1·47996, n_{H_γ} 1·48652, at 21·9°. *Tin tetraisobutyl* has m. p. −13°, b. p. 143°/16·5 mm., D_4^{23} 1·0540, n_{H_α} 1·47112, n_D 1·47423, n_{H_β} 1·48206, n_{H_γ} 1·48863, at 23°. *Tin triisobutylisoamyl* has b. p. 152·9°/16·5 mm., $D_4^{26\cdot8}$ 1·0356, n_{H_α} 1·46851, n_D 1·47174, n_{H_β} 1·47984, n_{H_γ} 1·48575, at 26·8°.

*Tin diethyl-*n*-propyl chloride* has b. p. 108°/17 mm., $D_4^{15\cdot7}$ 1·3848, n_{H_α} 1·50207, n_D 1·50580, n_{H_β} 1·51524, n_{H_γ} 1·52322, at 15·7°. *Tin diethylisoamyl chloride* has b. p. 125·5—126·5°/13 mm., $D_4^{19\cdot9}$ 1·2994, n_{H_α} 1·49443, n_D 1·49805, n_{H_β} 1·50687, n_{H_γ} 1·51443, at 19·9°. *Tin diethyl-*n*-propyl bromide* has b. p. 112·2°/16 mm., D_4^{21} 1·5910, n_{H_α} 1·51759, n_D 1·52177, n_{H_β} 1·53232, n_{H_γ} 1·54129, at 21°. *Tin diethylisobutyl bromide* has b. p. 122°/17 mm., D_4^{20} 1·5108, n_{H_α} 1·51194, n_D 1·51586, n_{H_β} 1·52609, n_{H_γ} 1·53464, at 20°. *Tin diethylisoamyl bromide* has b. p. 137·5°/17 mm., D_4^{17} 1·4881, n_{H_α} 1·51251, n_D 1·51651, n_{H_β} 1·52653, n_{H_γ} 1·53503, at 17°. *Tin ethyldiisobutyl bromide* has b. p. 130·6°/13 mm., $D_4^{19\cdot5}$ 1·4085, n_{H_α} 1·50452, n_D 1·50837, n_{H_β} 1·51799, n_{H_γ} 1·52607, at 19·5°. *Tin ethyldiisoamyl bromide* has b. p. 154—155/16 mm., D_4^{20} 1·3650, n_{H_α} 1·50263, n_D 1·50631, n_{H_β} 1·51562, n_{H_γ} 1·52347, at 20°.

All densities are reduced to vacuum standard, and optical constants at higher temperatures are also recorded in one or two instances.

J. C. W

Hexa-alkyldistannanes. Atomic Linking of Tin. GERHARD GRÜTTNER (*Ber.*, 1917, **50**, 1808—1813).—Hexa-alkyldistannanes, $R_3Sn\cdot SnR_3$, are prepared by heating tin trialkyl bromides, diluted with an equal volume of ether, with sodium powder at 120°. They are colourless, highly refractive and dispersivo liquids with very unpleasant, penetrating odours. They are stable towards heat and are only slowly oxidised on exposure to the air.

Hexaethyldistannane has b. p. 161—162°, $D_4^{17\cdot8}$ 1·3795, n_{H_α} 1·53224, n_D 1·53738, n_{H_β} 1·55065, n_{H_γ} 1·56210, at 17·8°. *Hexa-*n*-propyldistannane* has b. p. 148·6°/15 mm., $D_4^{19\cdot5}$ 1·2436, n_{H_α} 1·52122,

n_D 1·52583, $n_{H\beta}$ 1·53773, $n_{H\gamma}$ 1·54806, at 19·5°. *Hexa*iso*butyldistannane* has b. p. 179°/3·5 mm., m. p. 43·8°, D_4^{59} 1·1330, $n_{H\alpha}$ 1·49706, n_D 1·50128, $n_{H\beta}$ 1·51191, $n_{H\gamma}$ 1·52120, at 59°. s.-*Tetraethyldi*-n-*propyldistannane*, $Sn_2Et_4Pr^{\alpha}{}_2$, has b. p. 165·8°/15 mm., D_4^{20} 1·3313, $n_{H\alpha}$ 1·53042, n_D 1·53541, $n_{H\beta}$ 1·54822, $n_{H\gamma}$ 1·55945, at 15·3°. s.-*Tetraethyldi*iso*butyldistannane* has b. p. 179°/15·5 mm., $D_4^{19\cdot8}$ 1·2919, $n_{H\alpha}$ 1·52108, n_D 1·52571, $n_{H\beta}$ 1·53772, $n_{H\gamma}$ 1·54815, at 19·8°.

Densities are reduced to vacuum standard. J. C. W.

Side-chain Chlorine Derivatives of Toluene (Benzyl anc Benzylidene Chlorides and Benzotrichloride). H. D. GIBB and G. A. GEIGER (U.S.-P., 1246739, 1917; from *J. Soc. Chem Ind.*, 1918, **37**, 52A).—Gaseous toluene and chlorine are introducec into a suitable reaction chamber in which they are subjected t the action of ultra-violet rays. One mol. of toluene with one two, or three mols. of chlorine produces benzyl chloride, benzyliden chloride, and benzotrichloride, respectively. W. P. S.

Bromination of *p*-Nitrotoluene. J. F. BREWSTER (*J. Amer Chem. Soc.*, 1918, **40**, 406—407).—In view of the usefulness o *p*-nitrobenzyl bromide in the characterisation of acids and phenol (see Reid, A., 1917, i, 333), it is of interest to know that satis factory yields of the reagent can be obtained by gradually addin bromine dissolved in carbon tetrachloride to a boiling solution o *p*-nitrotoluene, containing a trace of iodine, and exposed to sun light. [See also *Ind.*, April.] J. C. W.

Sulphonation of Aromatic Hydrocarbons or their Derivatives. H. BULL (U.S.-P., 1247499, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 52A).—The sulphonation is carried out in the presence of an organic solvent of lower specific gravity than sulphuric acid in which the hydrocarbon and sulphonated substance are soluble. The solution of the sulphonated product is removed, and if this is done continuously, the process may be made continuous. The solvent may consist of an excess of the aromatic hydrocarbon. W. P. S.

Tolane Chlorides from Calcium Carbide, Chlorine, and Benzene. CLINTON DAVIDSON (*J. Amer. Chem. Soc.*, 1918, **40**, 397—400).—If powdered calcium carbide, free from iron, is added to cold benzene saturated with chlorine a reaction slowly sets in, the mixture becomes warm, and hydrogen chloride is evolved. After a time, the action subsides, even while much chlorine still remains. If the solution is then chilled, it deposits a mixture of the stable and labile forms of tolane dichloride, but if it is heated for several days until the b. p. rises to 100°, it will then give much tolane tetrachloride. Toluene reacts somewhat more readily, and apparently in the same way.

The mechanism of the process is indicated as follows:

$$CaC_2 + Cl_2 \longrightarrow CCl{:}CCl;$$

this $+ 2C_6H_6 \longrightarrow$ CPh:CPh, and this $+ Cl_2 \longrightarrow$ CPhCl:CPhCl and $CPhCl_2 \cdot CPhCl_2$. [See also *Ind.*, April.] J. C. W.

Coloured Condensation Products of Fluorene and Aldehydes. LUIS GUGLIALMELLI and ANGELES DELMON (*Anal. Soc. Quim. Argentina*, 1917, **5**, 124—130. Compare following abstract).—An account of colorations obtained by the action of fluorene in chloroform solution on aliphatic and cyclic aldehydes.

A. J. W.

Chromatic Reactions of Fluorene and Carbohydrates. LUIS GUGLIALMELLI and ANGELES DELMON (*Anal. Soc. Quim. Argentina*, 1917, **5**, 169—176. Compare preceding abstract).—Solutions of fluorene in chloroform and in alcohol give characteristic colour reactions with monoses, polyoses, polyhydric alcohols, and glucosides. A. J. W.

Addition of Ethyl Sodioacetoacetate to the Aromatic Mustard Oils [Thiocarbimides]. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1918, **40**, 415—423).—Ethyl sodioacetoacetate reacts readily with phenyl-, the three tolyl-, *p*-bromophenyl-, and *β*-naphthyl-thiocarbimides according to the equation

$$Na \cdot CHAc \cdot CO_2Et + R \cdot N:C:S = CH_3 \cdot CO \cdot CH(CO_2Et) \cdot C(SNa):NR.$$

The *products change into thioanilides*, $NHR \cdot CS \cdot CHAc \cdot CO_2Et$, *on* acidifying with hydrochloric acid. In the case of the phenyl, para-substituted phenyl, and naphthyl compounds, these compounds suffer "acid hydrolysis" even with dilute alkali hydroxides, giving the fragments $NHR \cdot CS \cdot CH_2 \cdot CO_2H$, AcOH, and EtOH, but the *o*- and *m*-tolyl compounds undergo "ketonic hydrolysis," yielding alcohol, carbon dioxide, and the substances $CH_2Ac \cdot CS \cdot NH \cdot C_6H_4Me$. Ethyl and benzyl derivatives of ethyl sodioacetoacetate react with phenylthiocarbimide less readily, and the products are more stable towards alkalis.

Ethyl sodioacetoacetate, obviously prepared in a non-hydroxylic solvent (ether), and phenylthiocarbimide yield *ethyl acetylthionmalonanilate*, $NHPh \cdot CS \cdot CHAc \cdot CO_2Et$, which crystallises in pale yellow, prismatic needles, m. p. 82—83°, yields hydrogen sulphide, ethyl acetate, and aniline hydrochloride when boiled with concentrated hydrochloric acid, and silver sulphide and acetaldehyde with warm silver nitrate, and changes into malonthionanilic acid, $NHPh \cdot CS \cdot CH_2 \cdot CO_2H$ (Ruhemann, T., 1908, **93**, 624), on warming with sodium hydroxide.

o-Tolylthiocarbimide yields such an unstable primary product that it cannot be isolated. Ketonic hydrolysis takes place so readily that the product is *acetothionaceto*-o-*toluidide*,

$$COMe \cdot CH_2 \cdot CS \cdot NH \cdot C_6H_4Me,$$

which crystallises in nearly colourless needles, m. p. 73—75°, and is hydrolysed by concentrated hydrochloric acid to acetic acid and Wallach's thionaceto-*o*-toluidide, $CH_3 \cdot CS \cdot NH \cdot C_6H_4Me$ (the m. p. is

now given as 91—92° instead of 67—68°). *Acetothionaceto*-m-*toluidide* has m. p. 83—84°. *p*-Tolylthiocarbimide gives *ethyl acetylthionmalon*-p-*toluidate*, glistening, diamond-shaped tablets, m. p. 81° (the primary *sodium* derivative has m. p. 61—62°), and this yields *thionmalon*-p-*toluidic acid* on hydrolysis, in long, flat needles which melt at 97°, and change thereby into thionaceto-*p*-toluidide, m. p. 129·5—130·5° (Wallach).

Ethyl acetylthionmalon-p-*bromoanilate* has m. p. 81—83°; *thionmalon*-p-*bromoanilic acid* forms cream-coloured, flat needles and plates, and changes at 150° into p-*bromothionacetanilide*, which crystallises in narrow, hexagonal plates, m. p. 153°.

Ethyl acetylthionmalon-β-naphthylamate,

$$C_{10}H_7\cdot CS\cdot CHAc\cdot CO_2Et$$

(not purified), yields *thionmalon-β-naphthylamic acid*, in pale yellow plates, m. p. 87—89° (decomp.).

Ethyl sodio-α-ethylacetoacetate gives *ethyl α-acetyl-α-ethylthionmalonanilate* as an oil, which is much more stable towards acids and alkalis than the above analogues. Ethyl sodio-α-benzylacetoacetate reacts very sluggishly with phenylthiocarbimide, and the only product described is a *polymeride* of, apparently, β-phenylthionpropionanilide, $CH_2Ph\cdot CH_2\cdot CS\cdot NHPh$, having m. p. 222—223° (decomp.). J. C. W.

Unsaturated Groups in Chemical and Pharmacological Connexions. I. J. von Braun and Z. Köhler (*Ber.*, 1918, **51**, 79—96).—That the unsaturated radicle, allyl, differs in many respects from aliphatic radicles is well known. Chemically, the most striking differences are to be found in its weaker attachments to nitrogen (compare Collie and Schryver, T., 1890, **57**, 767; von Braun, A., 1900, i, 641; Komatsu, A., 1913, i, 39), halogens (Clarke, T., 1910, **97**, 416; von Braun, A., 1912, i, 433), and oxygen (Claisen and Eisleb, A., 1913, i, 1175). Pharmacologically, it is a striking fact that by the replacement of an *N*-methyl group by allyl in choline or codeine, bases are obtained which are antagonistic to the parent bases (A., 1917, i, 254; 1916, i, 665).

The question naturally arises, are these effects peculiar to allyl or are they reproduced by other unsaturated radicles, and, if so, is the position of the ethylene linking of moment? The problem has therefore been attacked, and so far the chemical influences of the cinnamyl, $-CH_2\cdot CH{:}CHPh$, the 2-furfuryl, $-CH_2\cdot C{<}\begin{array}{l}O-CH\\ CH{:}CH\end{array}$, and Δ^4-pentenyl, $-CH_2\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$, groups have been examined. It is found that the last resembles saturated radicles in its attachments, whilst the first two resemble allyl. An ethylene linking between the β- and γ-carbon atoms is therefore one factor of importance.

I. The Cinnamyl Radicle.—Cinnamyl bromide is conveniently prepared by heating cinnamyl alcohol with three times its weight of hydrobromic acid (D 1·48). The halogen is so loosely combined that it is quickly removed by warm water alone. The bromide

combines most readily with tertiary bases; for its behaviour with pyridine, see Clarke (*loc. cit.*); with trimethylamine, it forms *cinnamyltrimethylammonium bromide*, in silvery leaflets, m. p. 165°. It reacts vigorously with magnesium, the bromine being removed and αζ-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene formed. With magnesium ethyl iodide, it yields this diphenylhexadiene and also *α-phenyl-Δ^{α}-pentene*, b. p. 202—205°, D_4^{20} 0·8782, n_D^{20} 1·51575. It condenses with dimethylamine to form *cinnamyldimethylamine*,

$NMe_2\cdot CH_2\cdot CH{:}CHPh$,

as a colourless liquid with strong basic odour, b. p. 100—101°/7 mm., which forms a *picrate*, m. p. 110°.

II. THE 2-FURFURYL RADICLE.—Furfuraldehyde is converted by Schwabbauer's method (A., 1902, i, 230) into 2-furfurylmethylamine, b. p. 59—60°/25 mm., which forms a *benzoyl* derivative, b. p. 180—185°/5 mm., and reacts with ethyl iodide to give *2-furfurylmethylethylamine*, $NMeEt\cdot CH_2\cdot C{<}{\scriptsize\begin{matrix}O-CH\\ CH\cdot CH\end{matrix}}$. This is a colourless base which smells strongly like ammonia, has b. p. 69—70°/23 mm., forms a *picrate*, m. p. 91°, a *platinichloride*, m. p. 147°, and a *methiodide*, m. p. 101°, and reacts very vigorously with cyanogen bromide to give some *di-2-furfurylmethylethylammonium bromide*, $(C_4H_3O\cdot CH_2)_2NMeEtBr$, m. p. 151°, a little methylethylcyanamide, $CN\cdot NMeEt$, but also, in 80% yield, the desired *2-furfuryl bromide*. This is a very unstable oil, which severely attacks the mucous membrane, the skin, rubber, and cork, is quickly hydrolysed by warm water, and energetically combines with tertiary amines. *2-Furfuryltrimethylammonium platinichloride*, m. p. 146—148° (decomp.), is mentioned in this connexion.

2-Furfurylmethylamine combines with ethylene oxide at 50° to form *2-furfurylmethyl-β-hydroxyethylamine*,

$C_4H_3O\cdot CH_2\cdot NMe\cdot CH_2\cdot CH_2\cdot OH$,

as a glycerol-like liquid, b. p. 105°/6 mm., which yields a *picrate*, m. p. 68—70°, a very soluble *aurichloride*, a *platinichloride*, decomp. 133°, and a *methiodide*, m. p. 77—80°.

III. THE Δ^{δ}-PENTENYL RADICLE.—The parent substance in this series is the dimethylpentenylamine, $CH_2{:}CH\cdot[CH_2]_3\cdot NMe_2$, which is obtained by the Hofmann degradation of piperidine. This reacts very vigorously with cyanogen bromide, about half of the base being converted into its methobromide, and the remainder into *methyl-Δ^{δ}-pentenylcyanamide*, $CH_2{:}CH\cdot C_3H_6\cdot NMe\cdot CN$, b. p. 96—98°/7 mm. This is hydrolysed by boiling with 25% sulphuric acid to *methyl-Δ^{δ}-pentenylamine*, a mobile liquid, b. p. 107—109°, which fumes in the air, and forms a *platinichloride*, m. p. 158°, a *picrate*, m. p. 150°, and a *benzoyl* derivative, b. p. 164—167°/7 mm. This amide, $CH_2{:}CH\cdot C_3H_6\cdot NMeBz$, gives the desired Δ^{δ}-pentenyl haloids on fusion with phosphorus pentahaloids, but the yields are very small. Another attempt to prepare the haloids was therefore made.

A solution of sodium amyloxide is cautiously warmed with

αε-dichloropentane, when the di-ether, $C_5H_{10}(O\cdot C_5H_{11})_2$ (Hamonet, A., 1904, i, 705), and *ε-chlorodiamyl ether*, $C_5H_{11}\cdot O\cdot C_5H_{10}Cl$, are formed, the yield of the latter being 40%. This ether is a colourless, pleasant-smelling liquid, b. p. 100—105°/8 mm., which reacts with dimethylamine to form *dimethylamyloxyamylamine*, as a limpid liquid with penetrating odour, b. p. 99—103°/7 mm. [The amyloxy-residue in these compounds is derived from ordinary amyl alcohol; the prefix "g.-" is proposed, from Gärung = fermentation, to signify this.] The tertiary amine is hydrolysed by means of concentrated hydrochloric acid to *dimethyl-ε-chloroamylamine hydrochloride*, which is snow-white, and may be converted into the *aurichloride*, m. p. 64—65°. The free base is stable enough to be transformed into the *methiodide*, $C_5H_{10}Cl\cdot NMe_3I$, m. p. 134°, but this loses some chlorine as well as the iodine on treatment with silver oxide, so that on distilling the quaternary ammonium hydroxide only an impure specimen of the desired pentenyl chloride can be obtained.

The purest specimen of *Δ^δ-pentenyl bromide* so far obtained had b. p. 110°. It has a sweet odour, does not attack the eyes, is not readily attacked by water, does not combine easily with tertiary amines, but reacts fairly completely with magnesium, in all these respects differing from allyl bromide. Not sufficient magnesium Δ^δ-pentenyl bromide could be obtained in this way for any experiments, but the compound was prepared from αδε-tribromopentane, as follows.

ε-Phenoxyamyl iodide is treated with trimethylamine, the quaternary iodide is converted into the hydroxide, and this is distilled, when a 40% yield of *ε-phenoxy-Δ^α-pentene* is obtained as a pleasant-smelling, limpid liquid, b. p. 109—111°/13 mm., D_4^{20} 0·9464, n_D^{20} 1·50. The *dibromide* of this, b. p. 190—205°/12 mm., is hydrolysed by prolonged boiling with fuming hydrobromic acid to *αδε-tribromopentane*, which is a heavy oil, b. p. 128—132°/11 mm., with spicy odour. This behaves like other tribromides which contain two bromine atoms attached to neighbouring carbon atoms when treated with magnesium (A., 1911, i, 701, 938), the chief product being magnesium Δ^δ-pentenyl bromide, $CH_2{:}CH\cdot C_3H_6\cdot MgBr$. This is proved by the fact that Δ^ϵ-hexenoic acid, $CH_2{:}CH\cdot C_3H_6\cdot CO_2H$, is produced from it by the action of carbon dioxide (compare Fichter and Langguth, A., 1897, i, 590).

J. C. W.

Di*cyclo*hexylamine. Solid Hydrate and Alcoholate. GUSTAVE FOUQUE (*Compt. rend.*, 1918, **166**, 394—395).—Di*cyclo*hexylamine, when poured on to water at below 23°, gave a crystalline *hydrate*, $NH(C_6H_{11})_2,H_2O$, m. p. 23°. The solubility of the amine in water, and of water in the amine, diminished as the temperature rose above 23°. An equimolecular mixture of di*cyclo*hexylamine and ethyl alcohol at the ordinary temperature gave the *alcoholate*, $NH(C_6H_{11})_2,EtOH$, m. p. 28°, which dissociated in the air.

W. G.

Oxalyl Chloride as a Reagent in Organic Chemistry. II. Preparation of Aromatic Anhydrides. Reaction with Alcohols. ROGER ADAMS, W. V. WIRTH, and H. E. FRENCH (*J. Amer. Chem. Soc.*, 1918, **40**, 424—431. Compare A., 1916, i, 140; 1917, i, 4).—When slightly more than one molecular proportion of oxalyl chloride is added to a boiling solution of two parts of an aromatic acid in benzene, very good yields of the acid anhydride are obtained. The reaction apparently proceeds in two stages, thus: $2R\cdot CO_2H + C_2O_2Cl_2 = 2HCl + (R\cdot CO\cdot O)_2C_2O_2$, and this $= (R\cdot CO)_2O + CO + CO_2$, for *m*-nitro-, 2:4- and 3:5-dinitro-benzoic acids yield the intermediate mixed anhydrides (probably owing to the insolubility of these in benzene), which decompose in the indicated way on heating or on treatment with cold pyridine.

The advantages of the method are obvious. The following anhydrides have been prepared in this way: benzoic; the three toluic; o-*chlorobenzoic*, white, prismatic needles, m. p. 78—79°; *m-chlorobenzoic*, short, white needles, m. p. 95°; *p*-chlorobenzoic; m-*iodobenzoic*, plates, m. p. 134°; *o*-nitrobenzoic; m-*nitrobenzoic oxalic anhydride*, $(NO_2\cdot C_6H_4\cdot CO\cdot O)_2C_2O_2$, pale yellow, decomposing at 157° into m-*nitrobenzoic anhydride*, m. p. 163° [Autenrieth's anhydride, m. p. 47° (A., 1901, i, 186), was really Greene's *m*-nitrobenzoic acetic anhydride, $Ac\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$ (A., 1890, 53)]; 3:5-*dinitrobenzoic oxalic anhydride*, decomp. 175°, and 3:5-*dinitrobenzoic anhydride*, m. p. 109°; 2:4-*dinitrobenzoic oxalic anhydride*, m. p. 205—209° (decomp.), and 2:4-*dinitrobenzoic anhydride*, m. p. 160°.

Just as phenols react with oxalyl chloride in the presence of pyridine, at 0°, to form oxalates, so primary and secondary alcohols give these esters in 50% yield, on an average. Tertiary alcohols usually do not react at all. The following *oxalates* have been prepared by this method: *benzhydryl*, m. p. 142—143°; *phenyl-o-tolylcarbinyl*, $(CHPh\cdot C_6H_4Me)_2C_2O_4$, m. p. 86—87°; *benzoin oxalate*, $(COPh\cdot CHPh)_2C_2O_4$, m. p. 243—245°; *piperonoin oxalate*, $C_{34}H_{26}O_8$, m. p. 225—226°; bornyl; menthyl; *iso*propyl; and *diphenylmethylcarbinyl oxalate*, $(CMePh_2)_2C_2O_4$, pyramids, decomp. 170—185° (yield very small). [See also *Ind.*, April.]

J. C. W.

Preparation of Solutions of Glycol Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 298185, 1915; from *Chem. Zentr.*, 1917, ii, 145).—Ethylene glycol monobenzoate, m. p. 45°, can be dissolved in almost any proportion in solutions of the alkali salts of benzoic, toluic, salicylic, or cresotic acid; in place of the benzoyl derivative of ethylene glycol, the corresponding *m*- and *p*-toluoyl, *o*-chlorobenzoyl, or salicyl compound may be used.

D. F. T.

Preparation of Acyl Derivatives of Aromatic Amides. MENDEL PERELSTEIN and EMIL BÜRGI (D.R.-P., 297875, 1915; from *Chem. Zentr.*, 1917, ii, 144—145).—By introducing the *iso*valeryl radicle into the amino-group of aromatic amides, compounds are

obtained possessing the soporific power of the amides, but much less poisonous. The method of preparation is by the direct interaction of the *iso*valeryl haloid with the acid amide, either in the molten condition or dissolved in an organic solvent in the presence of a dehydrating agent. By brominating the *iso*valeryl-substituted amide or by using an α-bromo*iso*valeryl haloid for the first reaction, it is possible to produce compounds of especial therapeutic value. The following substances were obtained: *cinnamoyl-α-bromo*isovaleryl*amide*, colourless needles, m. p. 118° (*dibromide*, crystals, m. p. 145° with reddening); *benzoyl-α-bromo*isovaleryl*amide*, colourless needles, m. p. 142—143°; *bis-α-bromo*isovaleryl*salicylamide* [*α-bromo*isovalero*xybenzoyl-α-bromo*isovaleryl*amide*], needles, m. p. 119°; *benzoyl*isovaleryl*amide*, needles, m. p. 89°; *cinnamoyl*isovaleryl*amide*, needles, m. p. 103° (*dibromide*, m. p. 165°). D. F. T.

The Walden Inversion. VI. Influence of the Solvent on the Sign of the Product in the Conversion of Phenylbromoacetic Acid into Phenylaminoacetic Acid. GEORGE SENTER and STANLEY HORWOOD TUCKER (T., 1918, **113**, 140—151; compare A., 1915, i, 535; 1916, i, 815; 1917, ii, 301).—It was found in the first experiments of this series that the sign of the amino-acid obtained by the action of ammonia on active phenylchloroacetic acid depends on the nature of the solvent employed, and it appeared to be of interest to examine this phenomenon in other cases.

Experiments on the displacement of bromine by the amino-group in the case of *l*-phenylbromoacetic acid have given the following results: (*a*) in aqueous solution, or in the higher alcohols (*n*-butyl, trimethylcarbinol, *n*-heptyl), the amino-acid obtained is opposite in sign, which agrees with the behaviour of phenylchloroacetic acid; (*b*) in the lower alcohols (methyl, ethyl, *n*- and *iso*-propyl) the product is also opposite in sign, whereas the amino-acid obtained from phenylchloroacetic acid in these solvents has the same sign as the parent halogeno-acid; (*c*) in acetonitrile or liquid ammonia, the product has the same sign, as in the earlier case; (*d*) considerable racemisation takes place in the lower alcohols, but not in the higher; (*e*) the presence of ammonium bromide has little racemising influence in aqueous solution, but considerable in liquid ammonia; (*f*) small quantities of iminodiphenyldiacetic acid, of high activity, opposite in sign to the original acid, are formed in all solvents.

The mechanism of the formation of the imino-acid is discussed. It is probable that it is formed by the direct action of ammonia on two molecules of the halogeno-acid, rather than by the interaction of the halogeno-acid with the amino-acid. J. C. W.

The Walden Inversion. VII. Influence of the Solvent on the Sign of the Product in the Conversion of α-Bromo-β-phenylpropionic Acid to α-Amino-β-phenylpropionic Acid (Phenylalanine). Iminodiphenyldipropionic Acid. GEORGE SENTER, HARRY DUGALD KEITH DREW, and GERALD HARGRAVE MARTIN (T., 1918, **113**, 151—163).—α-Bromo-β-phenylpropionic

acid has been examined in this series as the phenyl group is removed from the asymmetric carbon atom, and consequently different results might perhaps be anticipated. *It is found that in all the solvents* tried, water, alcohols, and even acetonitrile and liquid ammonia, the amino-acid has the opposite sign to the parent active acid, although very considerable racemisation occurs in the last two media. The most remarkable difference between this case and the earlier ones is, however, that ammonium bromide actually lessens racemisation when the reaction is carried out in liquid ammonia.

a-Imino-ββ-diphenyldipropionic acid, $NH[CH(CH_2Ph)\cdot CO_2H]_2$, is formed in small amounts in all the solvents, with the same sign as the bromo-acid.

The perplexing differences observed in the three cases (papers V., VI., and VII.) are perhaps best accounted for on the assumption that the action of ammonia on the halogeno-acids proceeds as two simultaneous reactions, the formation of both *d*- and *l*-amino-acids. Which of these reactions predominates depends on the nature of the acid, the nature of the solvent, and other factors.

[For experimental details, see the original.] J. C. W.

Preparation of a Solid *iso*Valeric Acid Compound Soluble in Water. HUGO VOSWINCKEL (D.R.-P., 294877, 1914; from *Chem. Zentr.*, 1917, ii, 144).—By warming a mixture of *iso*valeryl chloride and mandelic acid in benzene solution, *isovaleryl-mandelic* [*a-isovaleryloxyphenylacetic*] *acid*,

$$C_4H_9\cdot CO\cdot O\cdot CHPh\cdot CO_2H,$$

hard crystals, m. p. 71°, is obtained, the *calcium* salt of which is a granular solid soluble in water. D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. V. Some Derivatives of Tetrachloro- and Tetraiodo-phthalimides. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 198—214. Compare A., 1914, i, 415; 1915, i, 686, 692).—In the hope of obtaining a clearer insight into the relationship between the absorption bands shown by various members of the same family and a more exact knowledge of the origin of each band, investigation is being made of the absorption spectra of a large number of compounds related to phthalic acid, each differing only slightly from its neighbours. The present paper only deals with the preparation of phthalic acid derivatives in which halogen is substituted into the benzene ring, or in which the anhydride oxygen is replaced.

Tetrachlorophthalic anhydride, prepared by the action of chlorine on a hot solution of phthalic anhydride in fuming sulphuric acid in the presence of iodine, gives unstable, deeply coloured additive compounds with certain amines; with dimethylaniline and dimethyl-*p*-toluidine the *additive* compounds were isolated as red prisms, $C_8O_3Cl_4,NPhMe_2$, and almost purple crystals,

$$C_8O_3Cl_4,C_7H_7\cdot NMe_2,$$

respectively, but the formation of similar compounds with diethylamine, methylaniline, and the two naphthylamines could only be

detected by the red colour of mixtures of the anhydride and the respective bases, dissolved in xylene if necessary; diphenylamine and aniline yielded yellow solutions, whilst no colour change was observed with pyridine and triethylamine; the presence of chlorine is not essential to this reaction because 3-nitrophthalic anhydride and other substituted phthalic anhydrides, including, indeed, even phthalic anhydride itself, are capable of similar behaviour, the effect being so general as to suggest that the formation of such additive compounds is an essential first stage in the condensation of phthalic anhydride and its nuclear substituted derivatives with aromatic amines. In these additive compounds it is believed that the attachment between the two molecules occurs by means of residual valency at the anhydride oxygen atom and the nitrogen atom of the amine; with a tertiary amine no further change is possible, but with a secondary amine rearrangement subsequently occurs with formation of the colourless salt, whilst with a primary amine, such as aniline, the formation of the aniline phthalanilate can be succeeded by loss of aniline and production of the anil. In accordance with this view, the yellow solution of tetrachlorophthalic anhydride and aniline in benzene gradually deposits *aniline tetrachlorophthalanilate*, $C_{20}H_{14}O_3N_2Cl_4$, a colourless, crystalline powder, m. p. 271—273° (corr.), which readily undergoes further condensation to tetrachlorophthalanil, m. p. 274—275° (corr.). When tetrachlorophthalic anhydride is heated with aniline, preferably in an inactive atmosphere, the reaction goes still further with production of *3-anilino-4:5:6-trichlorophthalanil*, $C_{20}H_{11}O_2N_2Cl_3$, orange blades, m. p. 179·5—180·5° (corr.), and a *dianilinodichlorophthalanil*, $C_{26}H_{17}O_2N_3Cl_2$, bright, scarlet blades, m. p. 182·5—183·5° (corr.). *Tetrachlorophthal-o-tolil*, $C_{15}H_7O_2NCl_4$, colourless, rhombic leaflets, m. p. 232—236·5° (corr.), also its meta-*isomeride*, m. p. 245·5—246·5° (corr.), and para-*isomeride*, were obtained by heating a solution of tetrachlorophthalic anhydride and the corresponding toluidine in acetic acid. Tetrachlorophthal-*o*-tolil exhibits dimorphism, separating from acetic acid or alcohol in colourless, hexagonal leaflets, which at 207° (corr.) soften and become yellow with formation of a coloured modification, m. p. 214—214·5° (corr.); this is stable only above 118°, and can also be obtained in long, hair-like crystals by seeding the warm solution of the ordinary form in acetic acid or alcohol with a little of the yellow form. In accordance with the probability that the yellow form below its transition point must possess more free energy than the colourless modification, it is found that the former yields coloured *additive* compounds with benzene (3 or $4C_{15}H_7O_2NCl_4,C_6H_6$, long, yellow, hair-like crystals), *m*-xylene ($4C_{15}H_7O_2NCl_4,C_6H_4Me_2$), nitrobenzene ($4C_{15}H_7O_2NCl_4,C_6H_5\cdot NO_2$, yellow blades), and dimethylaniline ($5C_{15}H_7O_2NCl_4,NMe_2Ph$, scarlet needles), whereas the colourless variety shows no such tendency. The following anils were obtained by heating together the corresponding base and tetrachlorophthalic anhydride in acetic acid solution: *tetrachlorophthal-o-nitroanil*, $C_{14}H_4O_4N_2Cl_4$, colourless

leaflets, m. p. 272—273° (corr.); *tetrachlorophthal*-m-*nitroanil*, colourless blades, m. p. 300—301·5° (corr.); *tetrachlorophthal*-p-*nitroanil*, fine, colourless needles, m. p. 292—297° (corr.); *tetrachlorophthal*-p-*hydroxyanil*, $C_{14}H_5O_3NCl_4$, bright yellow needles, m. p. 305—307° (corr.); *tetrachlorophthal*-p-*acetylaminoanil*, pale yellow nodules or colourless needles, m. p. near 339° (corr.).

For the preparation of tetrachlorophthalimide, m. p. 338—339° (corr.), Graebe's method (*Annalen*, 1887, **238**, 332) is less convenient than one employing formamide in place of ammonia, a warm solution of the tetrachlorophthalic anhydride in the former rapidly depositing the imide. In a similar manner tetra-iodophthalic anhydride reacts with formamide, giving *tetraiodophthalimide*, $C_8HO_2NI_4$, fine, yellow needles, m. p. 370—380° (decomp.), whilst condensation of the anhydride with the various aromatic amines in nitrobenzene solution gives *tetraiodophthalanil*, $C_{14}H_5O_2NI_4$, yellow blades, m. p. 314—315° (corr.); *tetraiodophthal*-o-*tolil*, $C_{15}H_7O_2NI_4$, minute, yellow crystals, m. p. 314—315° (corr.); *tetraiodophthal*-m-*tolil*, yellow blades, m. p. 325—326°; *tetraiodophthal*-p-*tolil*, yellow blades, m. p. 317—318° (corr.); *tetraiodophthal*-m-*nitroanil*, $C_{14}H_4O_4N_2I_4$, yellow, matted needles, m. p. 318—319° (corr.); *tetraiodophthal*-p-*hydroxyanil*, $C_{14}H_5O_3NI_4$, fine, yellow needles, m. p. 330—336° (corr.), and *tetraiodophthal*-p-*acetylaminoanil*, minute, yellow blades, m. p. 339° (corr., decomp.). D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. VI. Action of Amines on Dichlorophthalic Anhydrides. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 214—218. Compare preceding abstract).—3:4-Dichlorophthalic acid reacts with aniline in boiling acetic acid solution, yielding 3:4-*dichlorophthalanil*, $C_{14}H_7O_2NCl_2$, which usually crystallises in very pale yellow, silky needles, m. p. 174° (corr.), but on account of the readiness of transformation into a second modification, colourless prisms, m. p. 182—182·5° (corr.), the lower m. p. can be observed only by sudden immersion of a small quantity of the needles in a bath near 174°. When heated with an excess of aniline in an inert atmosphere, the dichlorophthalic acid undergoes further conversion into 3-*anilino*-4-*chlorophthalanil*, $C_{20}H_{13}O_2N_2Cl$, orange leaflets, m. p. 159·5—160°. In a similar manner, 3:6-dichlorophthalic acid is convertible into 3:6-dichlorophthalanil, m. p. 197—198° (corr.), and 3-*anilino*-6-*chlorophthalanil*, $C_{20}H_{13}O_2N_2Cl$, which exhibits dimorphism, the crystals commonly obtained from alcohol forming orange needles, which on rapid heating have m. p. 141° (corr.), whereas on slow heating or on being kept in contact with the solvent the substance becomes changed into a second form, small, orange prisms, m. p. 160—160·5°. 4:5-Dichlorophthalic anhydride reacts with aniline in boiling acetic acid, yielding 4:5-*dichlorophthalanil*, colourless, rhombic leaflets, m. p. 212·5—213° (corr.), but shows no tendency to the further replacement of chlorine by the anilino-group. D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. VII. Di-iodo-, Tri-iodo-, and Dichloroiodo-phthalic Acids. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 219—236. Compare preceding abstracts).—In extension of the investigation in which chlorine in halogenated phthalanils was observed to be replaceable by the anilino-group, various iodophthalic acids were prepared for interaction with aniline.

When phthalic anhydride dissolved in fuming sulphuric acid is treated with iodine the composition of the product is dependent on the temperature; prolonged heating at 75° gives rise to nearly equal amounts of the 3:4- and 3:6-di-iodo-acids with much smaller quantities of 4:5-di-iodophthalic acid and 3:4:6-tri-iodophthalic anhydride, whereas the product obtained on rapid heating to 200° contains approximately the same amount of the 4:5-di-iodo-acid with a larger amount of the 3:4-di-iodo-acid and the tri-iodo-anhydride at the expense of the 3:6-di-iodo-acid. Traces of 4-iodophthalic acid and tetra-iodophthalic anhydride were also observed. A partial separation of the products is possible by esterification, only the 4:5-di-iodo-acid and part of the 3:4-di-iodo-acid forming normal esters with alcohol and hydrogen chloride. Separation was finally effected, however, by fractional precipitation from a solution of the disodium salts with acetic acid, causing deposition of the monosodium salts in the order 4:5-di-iodo-acid, tri-iodo-acid, and 3:4-di-iodo-acid, the salt of the 3:6-di-iodo-acid remaining in solution, aided by the knowledge that on recrystallisation from acetic acid the 3:4- and 4:5-di-iodo-acids separate unchanged, whereas the 3:6-di-iodo-acid and the tri-iodo-acid become converted into the corresponding anhydrides, which are very soluble in benzene. The structure of the various acids was determined by heating with sodium hydroxide solution and examination of the resulting hydroxy-acids. The dichlorophthalic anhydrides can be iodinated in a similar manner to the parent phthalic anhydride.

3:4-*Di-iodophthalic acid*, $C_8H_4O_4I_2$, colourless leaflets, m. p. 212—213° (corr.), when heated with acetic anhydride in benzene solution, yields the corresponding *anhydride*, $C_8H_2O_3I_2$, almost colourless prisms, m. p. 198—198·5° (corr.), is slowly hydrolysed by sodium hydroxide solution with formation of 3:4-dihydroxybenzoic acid, and reacts with aniline in boiling acetic acid, forming an *anil*, $C_{14}H_7O_2NI_2$, very pale yellow prisms, m. p. 270—271° (corr.).

3:6-*Di-iodophthalic acid* forms colourless leaflets which undergo gradual dehydration even below 100° with formation of the *anhydride*, colourless prisms, m. p. 234·5—235·5° (corr.). When heated with aqueous sodium hydroxide, 3-hydroxyphthalic acid is produced with much tarry matter, but no 3:6-dihydroxy-acid; however, by boiling a solution of the anhydride with aqueous pyridine and silver sulphate it is possible to obtain 6-*iodo-3-hydroxyphthalic anhydride* (*acetate*, $C_{10}H_5O_5I$, square crystals, m. p. 148·5—152·5°, corr.), which is hydrolysable with concentrated sodium hydroxide solution to 3:6-dihydroxyphthalic acid. 3-Hydroxyphthalic acid, $C_8H_6O_5$, colourless prisms, m. p. 161—163° (corr.; decomp.), readily passes into the anhydride, orange-yellow crystals, m. p. 198—199° (corr.;

Jacobsen, A., 1883, 1124, gives 145—148°), the *acetate* of which crystallises in colourless leaflets, m. p. 113·5—115·5° (corr.), and the *benzoate* in leaflets, m. p. 147·5—148° (corr.). 3:6-Di-iodophthalanil, prepared similarly to its 3:4-isomeride, forms colourless, rectangular plates, m. p. 233·5—234° (corr.).

4:5-*Di-iodophthalic acid*, colourless needles (probably with acetic acid of crystallisation) or leaflets, m. p. 221—222° (corr.; decomp.), on dehydration with acetic anhydride or by mere heating is converted into the *anhydride*, colourless prisms, m. p. 216·5—217° (corr.); hydrolysis of the acid with sodium hydroxide yields 4:5-dihydroxyphthalic acid and perhaps a little 3:4:5-trihydroxyphthalic acid. 4:5-*Di-iodophthalanil*, prepared by heating the acid with acetic anhydride and aniline in acetic acid solution, exhibits dimorphism, separating from acetic acid or xylene in pale yellow needles, which on rapid heating have m. p. 231·5—233° (corr.), but on gradual heating undergo transformation into a modification, m. p. 241·5—243° (corr.), the latter being also obtained in the form of pale yellow, hexagonal leaflets from the molten anil on very slow cooling.

3:4:6-*Tri-iodophthalic anhydride*, $C_8HO_3I_3$, bright yellow, rhombic pyramids, m. p. 230—231° (corr.), yields an *anil*, $C_{14}H_6O_2NI_3$, light yellow, microscopic needles, m. p. 254·5—255·5° (corr.), and on hydrolysis with sodium hydroxide gives a mixture of 3:6-dihydroxyphthalic acid with other substances, probably including a little 3:5-dihydroxybenzoic acid.

3:4-*Dichloro-5:6-di-iodophthalic anhydride*, $C_8O_3Cl_2I_2$, yellow prisms, m. p. 229·5—230·5° (corr.), obtained by the interaction of 3:4-dichlorophthalic anhydride and iodine in heated fuming sulphuric acid, yields an *anil*, $C_{14}H_5O_2NCl_2I_2$, pale yellow needles, m. p. 242·5—243·5° (corr.). 3:6-*Dichloro-4:5-di-iodophthalic anhydride*, yellow prisms, m. p. 258—258·5° (corr.), obtained in a similar manner, yields an *anil*, pale yellow needles, m. p. 232—232·5° (corr.). 4:5-*Dichloro-3:6-di-iodophthalic anhydride*, yellow blades, m. p. 232—233·5° (corr.), forms an *anil*, very pale yellow needles, m. p. 282·5—284° (corr.), and when heated with excess of aniline for twenty-four hours at 130° undergoes further conversion into 4:5-*dichloro-3:6-dianilinophthalanil*,

$$C_{26}H_{17}O_2N_3Cl_2,$$

orange-red crystals, m. p. 181·5—185° (corr.), quite distinct from the isomeric product obtained by the action of aniline on tetrachlorophthalanil (this vol., i, 168). D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. XII. Tetrachlorophthaloxime and some of its Derivatives. David S. Pratt and Charlotte H. Miller (*J. Amer. Chem. Soc.*, 1918, **40**, 407—412. Compare preceding abstracts).—Unsubstituted phthaloxime exists in two chromoisomeric forms (A., 1912, i, 190), but only one colour has been observed with the tetrachloro- and tetraiodo-phthaloximes and their ethers and esters. The ethers of tetrachlorophthaloxime, however, often exist in two modifications,

usually cotton-like masses and stable, stout prisms, which are interchangeable, and this dimorphism has not been observed in the other series.

Tetrachlorophthaloxime (A., 1913, i, 100) forms a red *silver* salt, from which the following colourless ethers,

$$C_6Cl_4<\begin{matrix}CO\text{———}\\C(:N\cdot OR)\end{matrix}>O,$$

may be prepared: *methyl*, blades, m. p. 206°; *ethyl*, m. p. 160°; iso*propyl*, very thin, glistening plates or clusters of stout prisms, m. p. 146°; iso*amyl*, m. p. 244°; *allyl*, m. p. 186°; and *benzyl*, filaments only, m. p. 192°. The acetate (*ibid.*) and *benzoate*, pearly, diamond-shaped plates or stout prisms, m. p. 210°, are also obtained from the silver salt.

Tetrachlorophthalic anhydride phenylhydrazone,

$$C_6Cl_4<\begin{matrix}CO\text{———}\\C(:N\cdot NHPh)\end{matrix}>O,$$

from the anhydride, phenylhydrazine, and glacial acetic acid, crystallises in yellow plates, which rapidly pass into orange needles, m. p. 287°. All m. p.'s are "corrected." [See also *Ind.*, April.]

J. C. W.

Phthalic Acid Derivatives. Constitution and Colour. XIII. Tetra-iodophthaloxime and some of its Derivatives. DAVID S. PRATT and THOMAS B. DOWNEY (*J. Amer. Chem. Soc.*, 1918, **40**, 412—415).—Tetra-iodophthalic anhydride (this vol., i, 177) has been converted into *tetra-iodophthaloxime*,

$$C_6I_4<\begin{matrix}CO\text{———}\\C(:N\cdot OH)\end{matrix}>O,$$

which exists in only one form, long, lemon-yellow needles of no definite m. p. From the red *silver* salt, the *methyl*, *ethyl*, n-*propyl*, iso*propyl*, n-*butyl*, iso*amyl*, n-*octyl*, *allyl*, and *benzyl* ethers, and the *acetate* and *benzoate*, have been obtained. These all crystallise in more or less pale yellow needles, and also decompose without melting. [See also *Ind.*, April.] J. C. W.

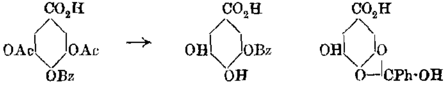
The Structure of Truxillic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 590—596).—From a consideration of their properties, their inter-conversion, and their preparation from cinnamic acids, the author has assigned spacial formulæ to the α-, β-, γ-, δ-, and ε-truxillic acids and to β-cocaic acid, on the assumption that these acids contain a tetramethylene ring. W. G.

New Synthesis of Digallic Acid, and Migration of Acyl in the Partial Hydrolysis of Acylated Phenolcarboxylic Acids. EMIL FISCHER, MAX BERGMANN, and WERNER LIPSCHITZ (*Ber.*, 1918, **51**, 45—79).—Two syntheses have already been described which were expected to lead to *p*-digallic acid, but yielded

m-digallic acid instead (A., 1908, i, 893; 1911, i, 875; 1913, i, 479). A third method is now described. 3:5-Diacetylgallic acid is condensed with *triacetylgalloyl chloride*, giving penta-acetyl-*p*-digallic acid, and this is cautiously hydrolysed by cold, dilute ammonia solution. Again, the surprising discovery has been made that the product is *m*-digallic acid.

Similarly, if 3:5-diacetylgallic acid is benzoylated and the acetyl groups are removed by hydrolysis, the product is not para-, but *m*-benzoylgallic acid, and when 4-benzoyloxy-3-acetoxybenzoic acid is partly hydrolysed, the product is 3-benzoylprotocatechuic acid.

All these unexpected products are therefore due to the wandering of one acyl group into the position vacated on hydrolysis by another attached to a neighbouring carbon atom. Thus:



(I.) (II.) (III.)

A transference of an acyl group has often been reported before, but only from carbon to oxygen or nitrogen and vice versa, or from nitrogen in a side-chain to nitrogen in the ring, numerous references to which are quoted, but this is the first record of such a migration from one phenolic group to another. The intermediate compound, (III), might perhaps be formed.

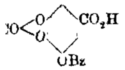
Derivatives of Gallic Acid.—Triacetylgallic acid is conveniently obtained by adding granulated zinc chloride (50 grams) to a mixture of gallic acid (500) and acetic anhydride (2500). If too much zinc chloride is used, considerable quantities of *triacetylgallic* [*3:4:5-triacetoxybenzoic*] *anhydride*, m. p. 175—176° (corr.), are formed as well. Pyridine and acetic anhydride may also be used. The acid has m. p. 171—172° (corr.), crystallises well, and forms a sparingly soluble silver salt and dark blue *copper* salt. The *chloride* is obtained in well-developed prisms, m. p. 106—107° (corr.), by the action of phosphorus pentachloride. The acid is hydrolysed to *3:5-diacetylgallic* [*3:5-diacetoxy-4-hydroxybenzoic*] *acid*, $C_{11}H_{10}O_7,H_2O$, stout spikelets, m. p. 174—175° (corr.), by dissolving it in the required quantity of concentrated potassium hydrogen carbonate solution, and slowly adding cold 2*N*-sodium hydroxide (1½ mols.), the mixture being kept below 0° and well stirred, and hydrogen being passed through without interruption. Some gallic acid and a *monoacetylgallic* [*acetoxydihydroxybenzoic*] *acid*, m. p. 225° (decomp.), are also formed, and a good deal of the triacetate escapes hydrolysis. The diacetate is methylated by means of diazomethane, the product being *methyl 3:5-diacetoxy-4-methoxybenzoate*, elongated tablets or prisms, m. p. 68—69°, which may be hydrolysed by cold, dilute sodium hydroxide in a current of hydrogen to the known 3:5-dihydroxy-4-methoxybenzoic

acid (gallic acid 4-methyl ether) (A., 1912, i, 559). This proves the constitution of the diacetate.

Penta-acetyl-p-*digallic acid* [4-(3′ : 4′ : 5′-*triacetoxybenzoyloxy*)-3 : 5-*diacetoxybenzoic acid*] is prepared by the interaction of triacetylgalloyl chloride and 3 : 5-diacetylgallic acid in cold, aqueous acetone in the presence of just sufficient dilute sodium hydroxide or potassium hydrogen carbonate. It forms thin needles, m. p. 202—203° (corr.), yields a *methyl* ester, m. p. 192—193° (corr.), and a *chloride*, m. p. 164—167° (corr.), and is hydrolysed by shaking with 5*N*-ammonia (8—9 mols.) in the cold, and in the absence of air, to *m*-digallic acid. This yields the methyl pentamethyl-*m*-digallate of definite constitution, and may also be shown not to be a para-derivative by the fact that on acetylation it yields a different penta-acetate. Penta-acetyl-*m*-digallic acid crystallises in stout prisms, m. p. 204—205° (corr.) (given in A., 1913, i, 479, as 193—194°), and forms a *methyl* ester, m. p. 167—168° (corr.). Similarly, the above methyl penta-acetyl-*p*-digallate yields *methyl* m-*digallate*, $1H_2O$, m. p. 175°, when cautiously hydrolysed by ammonia. This gives a bluish-black coloration with ferric chloride, and yields precipitates with pyridine, quinoline, brucine, and quinine salts; it may also be obtained by the action of dilute ammonia on methyl penta-acetyl-*m*-digallate, or converted into this by acetylation.

3 : 5-Diacetylgallic acid is benzoylated under the same conditions as observed in the above acylation. A small amount of a *benzoyloxyacetoxybenzoic acid*, $OH{\cdot}C_6H_2AcBz{\cdot}CO_2H$, m. p. 174—176° (corr.), is formed, but the main product is the desired 4-*benzoyl*-3 : 5-*diacetylgallic* [4-*benzoyloxy*-3 : 5-*diacetoxybenzoic*] *acid* (I). This crystallises in well-developed tablets or prisms, m. p. 183—184° (corr.), forms a *methyl* ester, m. p. 138—139° (corr.), and may be hydrolysed by means of 5*N*-hydrochloric acid in acetic acid at 85—90°, or by ammonia at 0°, or by warming with sodium acetate, the first being the best method, to 3-*benzoylgallic* [3-*benzoyloxy*-4 : 5-*dihydroxybenzoic*] *acid* (II), which has m. p. 240—242° (corr.), and gives a bluish-green colour with ferric chloride and a deep red with potassium cyanide. When treated with diazomethane, this yields *methyl* 3-*benzoyloxy*-4 : 5-*dimethoxybenzoate*, in stout tablets, m. p. 91—92°, which may be hydrolysed to the known 3-hydroxy-4 : 5-dimethoxybenzoic acid (3 : 4-dimethylgallic acid), m. p. 197—198° (corr.). Similarly, the above methyl 4-benzoyl-3 : 5-diacetylgallate may be converted into *methyl* 3-*benzoyloxy*-4 : 5-*dihydroxybenzoate*, stout plates or prisms, m. p. 173—175° (corr.), and this into the above ester, m. p. 91—92°, or into *methyl* 3-*benzoyloxy*-4 : 5-*diacetoxybenzoate*, elongated, flat, hexagonal tablets, m. p. 110—111°. 3-Benzoylgallic acid may also be reacetylated by means of pyridine and acetic anhydride, yielding the isomeric 3-*benzoyloxy*-4 : 5-*diacetoxybenzoic acid*, which crystallises in thin, curved needles, m. p. 177—178° (corr.), and may be esterified to the same ester as above (m. p. 110—111°), or hydrolysed again to 3-benzoylgallic acid.

4 : 5-Carbonylogallic acid (A., 1913, i, 479) yields 3-*benzoyloxy*-



4 : 5-*carbonyldioxybenzoic acid* (annexed formula) when shaken with benzoyl chloride and pyridine. This crystallises in thin, hexagonal tablets, m. p. 207—210° (corr.), and is hydrolysed to 3-benzoylgallic acid by boiling with acetone and water.

DERIVATIVES OF PROTOCATECHUIC ACID.—Protocatechuic acid is most conveniently acetylated by the method used in the case of gallic acid. The diacetylprotocatechuic acid [3 : 4-diacetoxybenzoic acid], m. p. 157—158° (corr.), is partly hydrolysed, also by the method applied to triacetylgallic acid, the product being 3-acetylprotocatechuic acid, m. p. 202—203° (corr.), apparently identical with an acid described by Ciamician and Silber in 1892. The constitution is proved by the fact that it is converted by diazomethane into methyl 3-acetoxy-4-methoxybenzoate, m. p. 87—88°, which may be hydrolysed to 3-hydroxy-4-methoxybenzoic acid (*iso*vanillic acid). 4-*Benzoyloxy*-3-*acetoxybenzoic acid* is obtained by benzoylation, in whet-stone forms, m. p. 154—155° (corr.). This yields a *methyl* ester, m. p. 102—103° (corr.), and may be hydrolysed by means of 5*N*-hydrochloric acid mixed with acetic acid, at 100°, to 3-*benzoyloxy*-4-*hydroxybenzoic acid*. This crystallises in microscopic needles, m. p. 225—227° (corr.), and forms *methyl* 3-*benzoyloxy*-4-*methoxybenzoate*, m. p. 101—102°, when treated with diazomethane, this being also obtained by benzoylating methyl *iso*vanillate. Similarly, the above methyl 4-benzoyloxy-3-acetoxybenzoate may be hydrolysed by ammonia to *methyl* 3-*benzoyloxy*-4-*hydroxybenzoate*, hexagonal tablets, m. p. 153·5—155° (corr.), which yields *methyl* 3-*benzoyloxy*-4-*acetoxybenzoate*, in long, thin prisms, m. p. 54—55°, on acetylation. J. C. W.

Phthalic Acid Derivatives. Constitution and Colour. VIII. Tetraiodofluorescein and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 236—245. Compare this vol., i, 168, 169, 170).—*Tetraiodofluorescein*, $C_{20}H_8O_5I_4$, obtainable from tetraiodophthalic anhydride and resorcinol by heating with zinc chloride, exists at the ordinary temperature as an unstable mixture of the benzenoid and quinonoid modifications. Its solutions in dilute aqueous alkali possess a yellowish-red colour and a vivid green fluorescence, and on acidification deposit a golden-yellow *hydrate*; this, when freshly precipitated, appears to contain loosely combined water, but after drying at the ordinary temperature in the air for a few days retains only approximately one molecule of water, for the removal of which a temperature of 120° is necessary; the first dehydration process does not affect the colour, but the passage into the anhydrous compound is accompanied by a change to reddish-brown, due to a partial conversion of the benzenoid into the quinonoid form; the hydrate is believed to be of the benzenoid structure. The application of a drop of acetone, alcohol, or ethyl acetate to the reddish-brown, anhydrous compound causes an immediate change of colour to a clear canary-yellow, due to rearrangement into the more stable benzenoid

modification. This behaviour is in marked contrast to that of fluorescein, which has never been isolated in the benzenoid condition. Treatment of the freshly precipitated tetraiodofluorescein with a little methyl or ethyl alcohol immediately converts it into the very pale yellow carbinol–carboxylic acid, the structural change being represented by the difference between formulæ I and II.

$$CO<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>C<\begin{matrix}-O-\\C_6I_4\end{matrix}>C(OH)_2$$

(I.)

$$CO<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>C(OH)\cdot C_6I_4\cdot CO_2H$$

(II.)

The anhydrous tetraiodofluorescein was also converted into the reddish-orange *potassium* salt, deep red *diammonium* salt, red *silver* salt, amorphous, bright red *methyl ether*, $C_{21}H_{10}O_5I_4$, decomp. near 251°, *diacetate*, $C_{24}H_{12}O_7I_4$, yellow crystals, and *dibenzoate*, $C_{34}H_{16}O_7I_4$, pale yellow crystals, m. p. 288° (corr.). D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. IX. Tetraiodoeosin and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 245—249. Compare preceding abstract).—Tetraiodofluorescein is readily brominated in acetic acid solution with formation of *tetraiodoeosin*, $C_{20}H_4O_5Br_4I_4$, canary-yellow crystals, which show no tendency to pass into a highly coloured quinonoid form, and are therefore presumably of benzenoid constitution. It dissolves in aqueous alkalis, yielding deep red solutions with faint green fluorescence, from which dilute hydrochloric acid precipitates a pink, amorphous *hydrate*, $3C_{20}H_4O_5Br_4I_4,H_2O$. Ammonia converts the solid tetraiodoeosin into a red *diammonium* salt,

$$C_{20}H_4O_5Br_4I_4,2NH_3,$$

whilst the *silver* salt, $C_{20}H_3O_5Br_4I_4Ag$, obtained by precipitation, is reddish-purple. *Tetraiodoeosin methyl ether*, $C_{21}H_6O_5Br_4I_4$, obtained by the action of methyl sulphate in the presence of alkali, is a red, amorphous powder, whilst the *diacetate*, $C_{24}H_8O_7Br_4I_4$, and *dibenzoate*, $C_{34}H_{12}O_7Br_4I_4$, form pale yellow crystals, m. p. 270—280° and near 261° respectively, with liberation of iodine in both cases. D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. X. Tetraiodoerythrosin (Octaiodofluorescein) and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 249—254. Compare preceding abstracts).—*Octaiodofluorescein*, $C_{20}H_4O_5I_8$, is most conveniently obtained by heating tetraiodofluorescein with iodine and iodic acid in alcoholic solution for twelve hours. When free from combined solvent, the compound forms clear, yellow crystals, but at 140° it becomes dark red, probably due to a transformation from the benzenoid to the quinonoid constitution. With acetone, it forms a yellow *additive* compound, $C_{20}H_4O_5I_8,C_3H_6O$, which is decomposed into its con-

stituents at 120°. Gaseous ammonia converts the solid *octaiodo*-fluorescein into a red *tetrammonium* salt, $C_{20}H_4O_5I_8,4NH_3$, whilst the *silver* salt, $C_{20}H_3O_5I_8Ag$, obtained by precipitation, is violet. The *methyl ether*, $C_{21}H_6O_5I_8$, prepared by the action of methyl sulphate, is an unstable, dark red, non-crystalline substance, whilst the *diacetate*, $C_{24}H_6O_7I_8$, and the *dibenzoate*, $C_{34}H_{12}O_7I_8$, form yellow crystals, decomp. above 200° and m. p. near 300° respectively.

D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. XI. Phenoltetraiodophthalein and some of its Derivatives. David S. Pratt and Asher F. Shupp (*J. Amer. Chem. Soc.*, 1918, **40**, 254—264. Compare preceding abstracts).—Tetraiodophthalic anhydride, yellow needles, m. p. 320—325° (corr.), obtained by heating phthalic anhydride and iodine with fuming sulphuric acid, when heated with an excess of phenol with the gradual addition of sulphuric acid, undergoes condensation with formation of phenoltetraiodophthalein, yellow crystals, m. p. 239—245° (compare Rupp, A., 1911, i, 301), which give a deep red solution in aqueous alkali. The phthalein is probably of benzenoid constitution, the yellow colour being attributed to the influence of the iodine atoms in bringing the absorption into the visible spectrum. It yields a *diacetate*, $C_{24}H_{14}O_6I_4$, pale yellow crystals, m. p. 230° (corr.), a *dibenzoate*, $C_{34}H_{18}O_6I_4$, pale yellow needles, m. p. 236° (corr.), a *dimethyl ether*, $C_{22}H_{14}O_4I_4$, yellow crystals, m. p. 221° (corr.), a *dinitro*-derivative, $C_{20}H_8O_8N_2I_4$, yellow needles, m. p. 311—312° (corr.) (*diacetate*, $C_{24}H_{12}O_{10}N_2I_4$, deep yellow crystals, m. p. 281°, corr.), a *tetranitro*-derivative, $C_{20}H_6O_{12}N_4I_4$, yellow crystals, decomp. near 311° (corr.), and a *tetrabromo*-derivative,

$$C_{20}H_6O_4Br_4I_4,$$

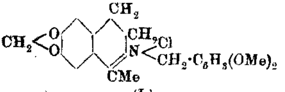
yellow crystals, m. p. 311—312° (corr.) (*diacetate*, $C_{24}H_{10}O_6Br_4I_4$, yellow crystals, m. p. 285°, corr.; *dibenzoate*, $C_{34}H_{14}O_6Br_4I_4$, yellow crystals, m. p. 213—215°, corr.; *dimethyl ether*, $C_{22}H_{10}O_4Br_4I_4$, yellow crystals, m. p. 255°, corr.). By treatment in cold aqueous alkaline solution with a solution of iodine in potassium iodide it is possible to convert phenoltetraiodophthalein into *tetraiodophenoltetraiodophthalein*, $C_{20}H_6O_4I_8$, deep yellow crystals, m. p. 285° (corr., with decomp.); this forms a *diacetate*, $C_{24}H_{10}O_6I_8$, pale yellow crystals, m. p. 288° (corr.), a *dibenzoate*, $C_{34}H_{14}O_6I_8$, pale yellow crystals, m. p. 202—203° (corr.), and a *dimethyl ether*, $C_{22}H_{10}O_4I_8$, pale yellow crystals, decomp. at 295—297° (corr.).

D. F. T.

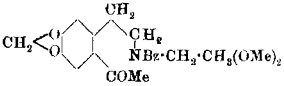
Laurent's Benzimide (Benzylidenebenzaldehydecyanhydrin-acetal). Maria Savelsberg (*J. pr. Chem.*, 1917, [ii], **96**, 186. Compare A., 1916, i, 728).—An acknowledgment of the priority of Stolle (A., 1902, i, 468) in the observation of the formation of an acetal compound by the condensation of mandelonitrile and benzaldehyde.

D. F. T.

Derivatives of Veratrole. ADOLF KAUFMANN and HERMANN MÜLLER (*Ber.*, 1918, **51**, 123—130).—I. DERIVATIVES OF *o*-VERATRALDEHYDE.—2 : 3-*Dimethoxybenzyl alcohol* (o-*veratryl alcohol*) is obtained by reducing the aldehyde with hydrogen and platinum-black; it crystallises in very long, massive, transparent, rectangular columns, m. p. 50°, and is converted into the *chloride*, b. p. 128·5—129°/11 mm., by means of thionyl chloride. The chloride rather easily loses hydrogen chloride on distillation under higher pressures, suffering condensation to an anthracene derivative. It also combines with methylnorhydrastinine, but the normal quaternary chloride (I) cannot be isolated, neither can the corresponding base. The solution, however, gives precipitates of a *perchlorate* and a *picrate*, m. p. 223—225°, whilst a *benzoyl* derivative, m. p. 146°, probably of the formula II, may be obtained by the Schotten-Baumann method.



(I.)



(II.)

Veratraldehyde and homopiperonylamine condense to form o-*veratrylidenehomopiperonylamine*, white needles, m. p. 59—60°, which may be hydrogenated in the presence of palladium-black to o-*veratrylhomopiperonylamine* (2 : 3-*dimethoxybenzyl*-β-3 : 4-*methylenedioxyphenylethylamine*),

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_3(OMe)_2,$$

a viscous oil, which forms a *hydrochloride*, $1H_2O$.

II. *p*-DERIVATIVES OF VERATROLE.—p-*Homoveratronitrile* (3 : 4-*dimethoxyphenylacetonitrile*) is obtained in long, colourless needles, m. p. 64—65°, b. p. 171—178°/10 mm., by heating the corresponding aldoxime with acetic anhydride.

ω - Bromoacetoveratrone [3 : 4 - dimethoxyphenyl bromomethyl ketone] (Mannich and Hahn, A., 1911, i, 649) reacts with potassium acetate in boiling alcohol to form the *acetate* (glistening tablets, m. p. 91—92°) of p-*veratroylcarbinol* (3 : 4-*dimethoxybenzoylmethyl alcohol*), which separates in transparent crystals, m. p. 86—87°.

III. DERIVATIVES OF DIMETHOXYBENZOIN.—Veratrole condenses with phenylacetyl chloride under the influence of aluminium chloride to form 3 : 4-*dimethoxydeoxybenzoin* (3 : 4-*dimethoxyphenyl benzyl ketone*) in white needles, m. p. 88°. A *bromide*, pale yellow crystals, m. p. 116—117°, is produced when the required quantity of bromine is carried by a stream of carbon dioxide into a solution of this in carbon disulphide, and *p*-toluenesulphonmethylamide reacts

with this bromide to form 3 : 4-*dimethoxyphenyl* α-p-*toluenesulphonylmethylaminobenzyl ketone*,

$C_6H_4Me{\cdot}SO_2{\cdot}NMe{\cdot}CHPh{\cdot}CO{\cdot}C_6H_3(OMe)_2$,

in white crystals, m. p. 180°. J. C. W.

The Beckmann Rearrangement. VIII. MITSURU KUHARA, NAOMICHI AGATSUMA, and KIUKICHI ARAKI (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1917, III, (1), *Reprint*, 16 pp.).—Kuhara and his colleagues have already shown that the esters of oximes derived from strong acids, for example, benzenesulphonates, spontaneously suffer the Beckmann rearrangement, whereas the addition of an acid like hydrochloric acid is necessary in order to bring about the change in esters of weak acids, like acetates. It is now suggested that the function of hydrochloric acid is to expel the weak acid, giving the oxime chloride which is immediately rearranged. Thus, in the case of diphenylketoxime acetate, the reaction is represented as follows: $CPh_2{:}N{\cdot}OAc + HCl \longrightarrow MeCO_2H + CPh_2{:}NCl \longrightarrow CPhCl{:}NPh$. It is impossible to isolate these chlorine derivatives, as the reaction proceeds further to the production of benzanilide, but if the acetate is heated with benzenesulphonic acid at 95—97°, an analogons product, phenylbenziminobenzenesulphonate (A., 1915, i, 144) may be recovered, thus:

$$CPh_2{:}N{\cdot}OAc + OH{\cdot}SO_2Ph \longrightarrow MeCO_2H + CPh_2{:}N{\cdot}O{\cdot}SO_2Ph \longrightarrow NPh{:}CPh{\cdot}O{\cdot}SO_2Ph.$$

The same idea may be applied in explaining the rearrangement of the hydrochlorides of oximes under the influence of dehydrating agents. The hydrochloride of diphenylketoxime changes instantly into benzanilide when heated at 128°, quickly when heated with zinc chloride or chloral at 90°, and within a day or two at 25° when mixed with chloral. The change is formulated thus:

$$CPh_2{:}N{\cdot}OH,HCl - H_2O \longrightarrow CPh_2{:}NCl \longrightarrow CPhCl{:}NPh \xrightarrow{H_2O} NHPh{\cdot}COPh.$$

In the case of the methyl ether hydrochloride, $CPh_2{:}N{\cdot}OMe,HCl$, methyl chloride is lost at above 45°, and no trace of the oxime suffers rearrangement, owing to the absence of the necessary :NCl group. The same interpretation is given to the rearrangement of diphenylketoxime by phosphorus pentachloride. If this agent is gradually added to an ethereal solution of the oxime, it first disappears, then the white hydrochloride of the oxime separates, and finally, when an equivalent has been added, a yellow chlorine compound is formed, which changes into benzanilide on adding water, thus: $2CPh_2{:}N{\cdot}OH + PCl_5 \longrightarrow CPh_2{:}NCl + CPh_2{:}N{\cdot}OH,HCl \xrightarrow[-H_2O]{+PCl_5} CPh_2{:}NCl$, and this $\longrightarrow NPh{:}CPhCl$.

What at first sight is a weak point in Kuhara's argument is the fact that chloroiminodiphenylmethane, $CPh_2{:}NCl$, when prepared by the action of hypochlorous acid on iminodiphenylmethane, resists the transforming influence of a large variety of agents (compare Stieglitz and Stagner, A., 1917, i, 22). If, however, the

chloro-imine is fused with potassium hydroxide, the rearrangement takes place with almost explosive violence, aniline and benzophenone being formed. The unsubstituted imine, and also diphenylketoxime and its acetate, do not yield aniline under the same treatment. The authors' explanation is that the chlorine atom in the stable chloro-imine is positively charged, and requires to be negatively charged before spontaneous rearrangement can take place, which alteration is brought about by the molten alkali, thus: $CPh_2:NCl^+ \xrightarrow{KOH} CPh_2:NCl^- \longrightarrow NPh:CPhCl^-$.

Evidence is also given to show that the ease with which the oxime esters undergo rearrangement is mutually dependent on the nature of the acid radicle and the hydrocarbon residues. Thus, the following benzenesulphonates suffer rearrangement at different temperatures: $CPh_2:NX$, 62°; $(CH_2Ph)_2C:NX$, 74°; $CMe_2:NX$, 130°; $CMePh:NX$, 81—82°; $\overset{OEt\cdot CPh}{\underset{NX}{\|}}$, 95—96°; whilst the following esters of diphenylketoxime vary in stability, according to the strength of the acid: $CPh_2:N\cdot O\cdot SO_2Ph$, 62°;

$CPh_2:N\cdot O\cdot SO_2\cdot C_6H_4\cdot NO_2(m)$, 24°;

$CPh_2:N\cdot O\cdot CO\cdot CH_2Cl$, above 195°; and $CPh_2:N\cdot OAc$, which does not change on heating. It appears, therefore, that the exchange of groups in the rearrangement is simultaneous.

Dibenzylketoxime benzenesulphonate (above) forms colourless crystals, m. p. 64°; the *acetate* has m. p. 33—34°, and the *benzoate*, m. p. 60·5°. *Diphenylketoxime* m-*nitrobenzenesulphonate* (above) has m. p. 24°, and the *chloroacetate* (above) also has m. p. 24°.

J. C. W.

Preparation of Dihydroxyanthraquinones and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 298345, 1916; from *Chem. Zentr.*, 1917, ii, 256).—It is possible to effect the condensation of phenols, naphthols, hydroxyanthracenes, and similar substances with phthalic anhydride under the influence of aluminium chloride with production of anthraquinone derivatives in one operation if the reaction mixture is heated at approximately 180—250°; it is advantageous to use an excess of phthalic anhydride to act as solvent. In this way catechol gives hystazarin free from alizarin, in considerably greater yield than when sulphuric acid is used; α-naphthol yields pure hydroxynaphthacenequinone, whilst β-naphthol gives hydroxynaphthanthraquinone, yellow needles. Hydroxyanthracenes and hydroxyanthraquinones reduced at the ketonic groups, for example, leucoquinizarin and deoxyalizarin, can also be condensed to hydroxyanthraquinone compounds. Pyrogallol yields anthragallol, yellow needles. The patent also refers to the formation of condensation products of phthalic anhydride with 1- and 2-hydroxyanthraquinones, 1:4:9:10-tetrahydroxyanthracene, deoxyalizarin, and 2:7-dihydroxynaphthalene, the product in the last case crystallising in yellow needles. 3:6-Dichlorophthalic acid and α-naphthol undergo condensation with

ormation of a compound crystallising in brown needles and soluble n sulphuric acid to a violet solution. D. F. T.

1 : 4 : 6-Trihydroxyanthraquinone. M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1918, **40**, 404—406).—4-Aminophthalic anhydride Bogert and others, A., 1902, i, 98; 1906, i, 510) condenses with quinol in concentrated sulphuric acid at 170—190° to form some 5-amino-1 : 4-dihydroxyanthraquinone (?), but chiefly 1 : 4 : 6-*trihydroxyanthraquinone*, which is a reddish-brown powder, not molten at 300°, and gives bluish-violet solutions in alkali hydroxides. It has no particular value as a mordant dye. [See also *Ind.*, April.] J. C. W.

Hydrogenation of Olefinic Terpene Alcohols, Aldehydes, and Acids. CARL PAAL (D.R.-P., 298193, 1913; from *Chem. Zentr.*, 1917, ii, 145—146).—Under suitable conditions it is possible to reduce alcohols, aldehydes, and acids of the terpene group by hydrogen and palladium or platinum, the ethylenic linking becoming hydrogenated, and two ethylenic linkings, if present, being capable of successive hydrogenation, without affecting the alcoholic, aldehydic, or acidic group. It is thus possible to reduce citral successively into citronellal and dihydrocitronellal; geraniol successively into citronellol and dihydrocitronellol; linalool successively into its dihydro- and tetrahydro-derivatives, and geranic acid successively into dihydrogeranic acid (*r*-citronellic acid) and tetrahydrogeranic acid. The palladium or platinum catalyst may be used in the colloidal condition, but for the present purpose the palladous or platinous hydroxide, or the metals themselves deposited on powders free from any anti-catalytic effect, are especially suited. A deposit of palladium or platinum may be formed on magnesium, nickel, or cobalt by immersing these metals in a solution of a palladium or platinum salt, or by treating precipitated magnesium oxide or carbonate or calcium carbonate with a solution of bivalent palladium or platinum it is possible to coat these powders with palladous or platinous hydroxide. Another method is to soak an indifferent powder, such as barium sulphate, infusorial earth, carbon, and cellulose powder with a solution of palladous or platinous salt, and then to precipitate the hydroxide of the rare metal on the powder by treating with sodium carbonate solution. With palladium or palladous hydroxide a convenient proportion of catalyst to carrier is 0·5—1%, whilst with platinum and its hydroxide it is 1—2%. D. F. T.

The Colouring Matters of Camwood, Barwood, and Sanderswood. PAULINE O'NEILL and ARTHUR GEORGE PERKIN (T., 1918, **113**, 125—140).—The well-known red dye-woods, sanderswood, barwood, caliaturwood, and camwood, are very similar in tinctorial properties. In fact, the first three might well contain the same pigment, but camwood dyes mordanted wool somewhat bluer tones and is more readily extracted by water. A chemical comparison of the camwood pigment with the santalin of

sanderswood, recently investigated by Cain and Simonsen (T., 1912, **101**, 1061), appeared to be desirable, and a preliminary account of a research in this connexion is now given.

The chief, more insoluble colouring matter of camwood is found to be an isomeride of santalin, designated iso*santalin*. It decomposes at a higher temperature than santalin (250—280°, as against 250—260°) and dyes bluer shades. For many reasons, both pigments are best expressed as $C_{22}H_{18}O_6(OMe)_2$, instead of $C_{14}H_{11}O_4(OMe)$. Both woods contain more soluble dyes, which are again isomeric. For these, the names *deoxysantalin* and *deoxy*iso*santalin*, and the formula $C_{22}H_{16 \text{ or } 18}O_5(OMe)_2$, are proposed. Not much can be said as to the relation between the santalins and the deoxysantalins, except that the results of acetylation do not indicate that the former possess one more hydroxyl group than the latter. The deoxysantalins are the better pigments.

The first pigment to be isolated from sanderswood was that obtained by Meier (1848), which is apparently deoxysantalin rather than santalin, although the present authors were not so successful in obtaining a crystalline specimen. In 1870, Weidel also obtained from sanderswood, santal, which is now written as $C_{15}H_9O_5{\cdot}OMe$, and a bright red substance, which is now designated *santalone*, and is possibly deoxysantalin monomethyl ether, $C_{22}H_{15}O_4(OMe)_3$. These are difficult to obtain from sanderswood, but they have now been extracted from barwood, which contains santalin as well. Santal crystallises in large, colourless leaflets, m. p. 222—223°, and yields *santol*, flat needles, m. p. 270—273°, on demethylation by Zeisel's method. Santalone forms glistening, red leaflets, m. p. 300°.

The colouring matter in the flower of St. John's wort is quercetin, and not gossypetin, as Keegan suggested (A., 1915, i, 758).

For experimental details, see the original. J. C. W.

The Mechanism of the Formation of certain Isomerides of Cinchonine and of their Hydrohaloid Derivatives. E. Léger (*Compt. rend.*, 1918, **166**, 255—258. Compare this vol., i, 121).—Admitting for cinchonine the constitution (formula I) and for cinchonigine and cinchoniline the constitution (formula II),

$$CH_2{:}CH{\cdot}C_{16}H_{17}N_2{:}CH(OH){\cdot} \quad \text{(I.)} \qquad \underset{O\text{————————}O}{CHMe{\cdot}[C_{16}H_{17}N_2{:}CH]} \quad \text{(II.)}$$

and for *apo*cinchonine, $CHMe{:}C_{16}H_{16}N_2{:}CH{\cdot}OH$, this latter being formed from cinchonine by the addition and subsequent removal of the elements of water, it is easy to see that the fixation of hydrogen bromide will in all four cases give the same hydrobromocinchonine. But the four compounds are optically active, and it must be supposed that the fixation of hydrogen bromide is preceded, in certain cases, by stereoisomeric changes. It is probable that cinchonine and cinchoniline have the

steric arrangement, their isomerism being due to differences of structure. In the cases of cinchonigine and *apo*cinchonine, there is a formation of their normal hydrobromo-derivatives, and at the same time a partial transformation into cinchoniline, which then yields hydrobromocinchonine. W. G.

A Synthesis of 2 : 6-Dimethylcinchomeronic Acid and 2 : 6-Lutidine. OTTO MUMM and HUGO HÜNEKE (*Ber.*, 1917, **50**, 1568—1584).—Some years ago, Mumm and Bergell found that the ammonium salt of acetylpyruvic acid gradually loses water to form 3-acetyl-4-methylpyridine-2 : 6-dicarboxylic acid, and this was explained on the assumption that the ammonium salt changes partly into an acid of the formula $CH_3 \cdot CO \cdot CH \colon C(NH_2) \cdot CO_2H$, which condenses with a further portion of the salt (A., 1912, i, 936). If this view is correct, it should be possible to effect such a pyridine synthesis, using other compounds of the type of acetylpyruvic acid on the one hand, and the above unsaturated amino-acid on the other. It is now shown that ethyl acetylpyruvate and ethyl β-aminocrotonate react vigorously at 0° to form ethyl 2 : 6-dimethylcinchomeronic acid, the constitution of which is revealed by the facts that the corresponding potassium salt yields 2 : 6-lutidine on distillation with lime, and that the free acid gives an anhydride.

Ethyl acetylpyruvate, which is obtained by Claisen's method from ethyl oxalate and acetone, reacts equally well with ethyl β-aminocrotonate at 0°, whether undiluted or mixed with alcohol or ether, giving a 90% yield of *ethyl* 2 : 6-*dimethylpyridine*-3 : 4-*dicarboxylate*, which is a pale yellow, viscous oil, b. p. 163°/13 mm., m. p. 16°, and gives a *hydrochloride*, quadratic tablets, m. p. 121°, a *picrate*, clusters of stout needles, m. p. 101°, and a *platinichloride*, yellow needles. If burnt in the ordinary way, the ester apparently forms a nitrogenous compound which escapes combustion, so nitrogen was determined by Kjeldahl's method and carbon and hydrogen by Dennstedt's process. If the mixture is not cooled, the water liberated during the condensation may cause two other reactions with the parent substances, thus:

$$NH_2 \cdot CMe \colon CH \cdot CO_2Et + H_2O = CH_2Ac \cdot CO_2Et + NH_3$$

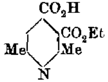
and $$CH_2Ac \cdot CO \cdot CO_2Et + NH_3 = CH_2Ac \cdot C(\colon NH) \cdot CO_2Et + H_2O.$$

That is, ethyl acetoacetate and *ethyl* α-*iminolaevulate* ("α-imide of ethyl acetylpyruvate" in the earlier paper) may be formed. The latter crystallises in thin prisms, m. p. 39°, b. p. 115°/13 mm.

The free 2 : 6-*dimethylpyridine*-3 : 4-*dicarboxylic acid* (2 : 6-*dimethylcinchomeronic acid*) crystallises by spontaneous evaporation of aqueous solutions in short, rhombic prisms, m. p. 275° (sealed capillary; decomp.). It is almost insoluble in most solvents. The *potassium* salt forms silky needles, and gives a 91% yield of 2 : 6-dimethylpyridine (2 : 6-lutidine), b. p. 142°, when distilled with calcium hydroxide, this being at present the most convenient method for making the pure lutidine. The acid also yields an *anhydride*, needles, m. p. 101°, when heated at 220°/vac., or with acetic

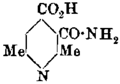
anhydride. It may be that Collie and Wilsmore were correct in a tentative suggestion that they had obtained the same acid by the oxidation of 8-hydroxy-1:3:6-trimethyl*iso*quinoline (T., 1896, **69**, 295).

If the diethyl ester is left with one equivalent of alcoholic potassium hydroxide, it is partly hydrolysed to the 3-*ethyl hydrogen ester* (annexed formula) small needles, m. p. 161°, whilst the anhydride dissolves in alcohol to form the 4-*ethyl hydrogen ester*, short, flat prisms, m. p. 151°.



On heating the ammonium salt of the acid at 230°, 2:6-*dimethylcinchomeronimide* sublimes in very long needles, m. p. 230°.

The diethyl ester reacts with alcoholic ammonia at 120° to form the *diamide*, slender needles, m. p. 220° (heating very rapidly; vigorous decomp.). The 3-*amic acid* (annexed formula), crystallising with $2H_2O$ in rhombic leaflets, is formed by dissolving the imide in 4*N*-sodium hydroxide, whilst the 4-*amic acid*, $2H_2O$, long needles, m. p. 115°, is obtained by saturating a benzene solution of the acid anhydride with ammonia. J. C. W.



Synthesis of some Pyridine-polycarboxylic Acids. OTTO MUMM and HUGO HÜNEKE (*Ber.*, 1918, **51**, 150—164).—The synthesis of 2:6-dimethylcinchomeronic acid (preceding abstract) opens up a convenient way to prepare tri- and tetra-carboxylic acids of pyridine.

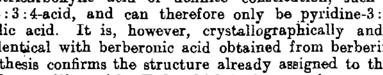
Oxidation of the acid with alkaline permanganate sufficient for one methyl group gives rise to a 67% yield of two methylpyridinetricarboxylic acids. The chief product is 2-*methylberberonic acid* (2-*methylpyridine*-3:4:6-*tricarboxylic acid*), which crystallises from water in stout, short, rhombic prisms, with $3H_2O$, decomp. 226° (anhydrous), and the lesser product is 6-*methylpyridine*-2:3:4-*tricarboxylic acid*, which forms long, thin prisms, or sometimes hexagonal tablets, and carbonises without obvious evolution of gas at 230—280°. The two acids differ in a remarkable way in their copper salts; the former gives a precipitate with cupric acetate in hot solutions, which dissolves on cooling, but the latter gives a precipitate in the cold, which dissolves on heating.

2-Methylberberonic acid loses carbon dioxide on heating with glacial acetic acid for some days, yielding 2-*methylpyridine*-3:4-*dicarboxylic acid*, in very long, thin prisms, m. p. 250—255°, which gives an *anhydride*, m. p. 92°, when boiled with acetic anhydride, this being also formed when the tricarboxylic acid is heated at 230° in a vacuum. The new dicarboxylic acid may be oxidised by alkaline permanganate to pyridine-2:3:4-tricarboxylic acid, which crystallises in thin, rectangular leaflets, $1·5H_2O$, m. p. 249°, and is identical with the acid obtained by the oxidation of cinchonine (Camps, A., 1902, i, 824).

Both methyl groups in the original acid may be oxidised if twice as much permanganate is used. The product is pyridine-2:3:4:6-tetracarboxylic acid, which crystallises from water in narrow tablets, $3H_2O$, m. p. 235°, and is identical with the acid prepared by Fischer and Täuber from flavenol (A., 1885, 400). When this is boiled with glacial acetic acid, it loses carbon dioxide and gives a tricarboxylic acid which is not identical with any pyridinetricarboxylic acid of definite constitution, such as the above 2:3:4-acid, and can therefore only be pyridine-3:4:6-tricarboxylic acid. It is, however, crystallographically and chemically identical with berberonic acid obtained from berberine, and this synthesis confirms the structure already assigned to this acid. The acid crystallises with $2H_2O$, which it does not lose on exposure to the air, and has m. p. 243° (decomp.). J. C. W.

The Relative Stability of Cyclic Bases. V. J. von Braun (*Ber.*, 1918, **51**, 96—100. Compare A., 1909, i, 604; 1911, i, 563; 1917, i, 168, 169).—Two very different methods have been worked out for effecting *the rupture of cyclic systems containing nitrogen*, namely, the Hofmann reaction and treatment with cyanogen bromide, but it has recently been shown that the gradations of stability exhibited by many of these bases are the same whichever test is applied. One exception seems to be dihydroindole, which proves to be one of the most stable systems in the Hofmann degradation, but one of the weakest towards cyanogen bromide.

1-Methyl-2:3-dihydroindole reacts with cyanogen bromide in the cold according to the scheme: $C_6H_4<{CH_2 \atop NMe}>CH_2 + BrCN \longrightarrow$
(1)

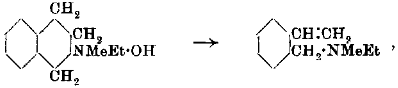


quaternary salts of (1) with (2) and (4) being formed as well, the yields being about 27% of (3) and 70% of (2), of which only 40% escapes the secondary reaction resulting in the quaternary salt. The quaternary salts are removed by ether as an insoluble, red oil, from which a small quantity of the *methobromide* of 1-methyldihydroindole, m. p. 195—197° (decomp.), may be recovered. The other bromide cannot be purified. The base (2) is characterised by warming the soluble products with dimethylamine dissolved in benzene, when it is converted into *cyanomethyl-o-β-dimethylaminoethylaniline*, $NMe_2 \cdot C_2H_4 \cdot C_6H_4 \cdot NMe \cdot CN$. This may be extracted from the benzene by dilute sulphuric acid; it is a pale yellow oil, b. p. 175—178°/16 mm., which exhibits pale green fluorescence in alcoholic solution, forms a *picrate*, m. p. 142°, a *platinichloride*, m. p. 144°, a *methiodide*, m. p. 170°, and may be hydrolysed by means of concentrated hydrochloric acid at 150° to *methyl-o-β-dimethylaminoethylaniline*,

$$NMe_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot NHMe.$$

This base is a pale yellow oil, b. p. 138—139°/15 mm., whicl forms a *picrate*, m. p. 165—166°, a *platinichloride*, $2H_2O$, m. p 218°, a *thiocarbamide*, m. p. 110°, and a *picrate* of its nitroso derivative, m. p. 139°. The remaining product, 1-*cyano*-2:3 *dihydroindole* (3), is recovered from the above benzene solutioi as a yellow liquid, b. p. 164—168°/23 mm. J. C. W.

Hydroxy-bases and Homologous Cholines. II. J. vo: Braun and Z. Köhler (*Ber.*, 1918, **51**, 100—108. Compare A. 1916, i, 631).—2-Methyltetrahydro*iso*quinoline forms an *ethiodid* m. p. 132—134°, which may be converted into the hydroxide When this is distilled under reduced pressure, the chief produc is o-*vinylbenzylmethylethylamine*, which has b. p. 105—107° 17 mm., and forms a *platinichloride*, m. p. 134°, and a *methiodid* m. p. 166—167°. The reaction,



illustrates once more the instability of the tetrahydro*iso*quinolin system (A., 1917, i, 169).

N-Methyldihydro*iso*indole is formed in small quantities by th interaction of *o*-xylylene dibromide and methylamine. It ha b. p. 81—82°/13 mm., and forms a *trihydrate*, m. p. 45—46° Other derivatives were described by Fränkel (A., 1901, i, 44) The ethiodide (Scholtz, A., 1898, i, 568) may be converted int methylethyldihydro*iso*indylium hydroxide, which suffers decon position in two ways on heating. The main product is *N*-methy dihydro*iso*indole, which is best removed by triturating the di tillate with water, when the above trihydrate is formed, bu o-*hydroxymethylbenzylmethylethylamine* is obtained as well, as colourless, viscous oil, b. p. 145—150°/16 mm., which darkens o exposure to the air and gives a deep red *platinichloride*, m. p 170°. The corresponding *dimethyldihydro*iso*indylium bromide* m. p. 238—240°, from o-xylylene dibromide and dimethylamine yields a hydroxide which behaves similarly on distillation. Mor than half of the product is o-*hydroxymethylbenzyldimethylamine* b. p. 130—132°/13 mm., the reaction being represented thus:

$$C_6H_4<{CH_2 \atop CH_2}>NMe_2{\cdot}OH \longrightarrow$$

$$C_6H_4<{CH_2 \atop CH_2}>NMe \text{ and } C_6H_4<{CH_2{\cdot}NMe_2 \atop CH_2{\cdot}OH}.$$

The new hydroxy-base forms an oily *picrate*, a *platinichloride* m. p. 168°, and an oily *benzoate*, which yields a *picrate*, m. p 159—160°, and it changes on heating with hydrochloric acid int *dimethyldihydro*iso*indylium chloride*, m. p. 198—200°.

The hydroxy-base may also be converted through th *methiodide*, m. p. 148—149°, into o-*hydroxymethylbenzyltri*

methylammonium chloride, $OH\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot NMe_3Cl$, m. p. 189°, which has exactly the same physiological activity as choline, and forms a *platinichloride*, m. p. 216°, and an *aurichloride*, m. p. .27°. The corresponding *allyliodide*, m. p. 123°, yields a chloride, which, like allylhomocholine, is antagonistic to choline.

These new hydroxy-bases and *o*-hydroxymethylbenzylpiperidine (A., 1917, i, 170) differ very characteristically from tertiary aminobenzyl alcohols of the type $OH\cdot CH_2\cdot C_6H_4\cdot NMe_2$ (A., 1916, i, 473, etc.). The former are colourless, the latter yellow, and whilst the latter are oxidised by formaldehyde in acid solutions, the former are quite stable towards this agent. J. C. W.

Synthesis of Cinchonic Acids. ADOLF KAUFMANN (*Ber.*, 1918, **51**, 116—122).—The cinchonic acids or their nitriles or esters seem to be the most favourable material from which to build up synthetic alkaloids of the cinchona group. Consequently, the synthesis of these acids from quinolines is a matter of importance, and therefore some new notes on the method originated by Kaufmann in 1909 (A., 1909, i, 958) are of interest.

The conversion of quaternary salts of the quinolines into 4-cyano-1-alkyl-1 : 4-dihydroquinolines by means of cold, aqueous potassium cyanide is best carried out in the presence of ether, which removes the unstable nitrile as fast as it is formed, either by dissolving it or by causing it to crystallise out. Quinoline itself gives a 75% yield, but substituted bases give better results. Thus, the methosulphate of 6-methoxyquinoline gives a very high yield of 4-cyano-6-methoxy-1-methyl-1 : 4-dihydroquinoline, m. p. 82° (A., 1912, i, 651). With the methiodides of various nitroquinolines, extremely fine crystals of the nitrile are deposited in a very short time; 5-*nitro*-4-*cyano*-1-*methyl*-1 : 4-*dihydroquinoline*, $NO_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{CH(CN)\cdot CH}{NMe—CH}}$, separates in large, pale yellow cubes or columns, m. p. 78° (decomp.); the 6-*nitro*-compound is a pale yellow, crystalline powder, m. p. 108° (decomp.); and the 8-*nitro*-compound forms large, yellow prisms, decomp. 90—92°; they all have the odour of hydrogen cyanide and are very easily oxidised, even decomposing with violence sometimes when brought from a desiccator into the air.

These nitriles may be oxidised by iodine to the methiodides of 4-cyanoquinoline (A., 1911, i, 749, 750). This is best carried out by dissolving the nitrile in pyridine and adding the solution quickly to an alcoholic solution of iodine (1 mol.). The yield of the quaternary salt varies from 90% for the unsubstituted quinoline product to 74% for the 6-methoxy-compound and 65% for the 6-ethoxy-derivative. The corresponding nitrile from hydrastinine and the above nitro-compounds react in a different way, being deprived of the cyano-group and reconverted into the parent methiodides.

The 4-cyanoquinoline methiodides are best converted into the 4-cyanoquinolines by heating alone (4-cyanoquinoline itself is

obtained in 90% yield) or with ethyl benzoate, the latter being the best treatment of the alkyloxy-derivatives. J. C. W.

The Diketopiperazines. IV. Attempts to Prepare 2 : 3-Diketo-1-phenylpiperazine. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1686—1692. Compare A., 1916, i, 635, 672).—When an aqueous solution of 1-nitro-3:5-diketopiperazine ("nitroiminodiacetimide," A., 1912, i, 753) is boiled, it deposits an indigo-blue, amorphous *compound*, probably of the formula $CO<{NH-CO \atop CH_2 \cdot NH}>C:C<{CO——NH \atop N(NO) \cdot CH_2}>CO$. This dissolves in sodium hydroxide to give a dark reddish-brown solution, which is bleached by sodium hyposulphite.

In order to obtain soluble sulphonic acids related to this insoluble product, the authors have made many attempts, described in this and in following abstracts, to prepare 2:3-diketo-1-phenylpiperazine, but so far without success.

In the first place, dichlorodiacetanilide, $C_6H_5 \cdot N(CO \cdot CH_2Cl)_2$, was required. All attempts to prepare this from aniline and chloroacetyl chloride or chloroacetic anhydride resulted in the formation of the monochloroacetanilide, whilst a condensation of phenylcarbimide with chloroacetic anhydride at 160—180° gave the same product mixed with 2:4-diketo-3-phenyltetrahydrothiazole,

$$NPh<{CO \cdot CH_2 \atop CO \cdot S}|,$$

m. p. 148°. J. C. W.

The Diketopiperazines. V. Action of Aniline on Methyl Iminodiacetate. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1692—1701).—In another attempt to prepare 2:3-diketo-1-phenylpiperazine, the authors have heated methyl iminodiacetate, or its hydrochloride, with aniline, in the hope of realising the reaction represented by equation (*a*). As a matter of fact, the reactions (*b*) and (*c*) are found to run concurrently.

(*a*) $NH(CH_2 \cdot CO_2Me)_2 + NH_2Ph =$
$$NH<{CH_2 \cdot CO \atop CH_2 \cdot CO}>NPh + 2MeOH.$$

(*b*) $NH(CH_2 \cdot CO_2Me)_2 + 2NH_2Ph =$
$$NH(CH_2 \cdot CO \cdot NHPh)_2 + 2MeOH.$$

(*c*) $2NH(CH_2 \cdot CO_2Me)_2 + 2NH_2Ph =$
$$4MeOH + NHPh \cdot CO \cdot CH_2 \cdot N<{CO \cdot CH_2 \atop CH_2 \cdot CO}>N \cdot CH_2 \cdot CO \cdot NHPh.$$

Iminodiacetonitrile (from hexamethylenetetramine and hydrogen cyanide) can be converted into methyl iminodiacetate hydrochloride in one operation (compare Jongkees, A., 1908, i, 959). 2:5-*Diketopiperazine*-1:4-*diacetanilide* (equation *c*) is not particularly soluble except in glacial acetic acid, from which it crystallises in pale grey, silky leaflets, m. p. 310—320° (decomp.). On hydrolysis, it yields the known 1:4-diacetic acid (*ibid.*). *Iminodiacetanilide* (*b*) is extracted from the product of the reaction by means of boiling water,

the mixture being slightly acidified by hydrochloric acid. It crystallises in glistening, long, snowy leaflets, m. p. 138—139°, the *hydrochloride* forms leaflets, m. p. 242° (decomp.), and the *nitrate*, stout needles, m. p. 182—183°. The salts are completely dissociated in water, but can be precipitated by the addition of the free acids or metallic salts in excess. The compound also reacts with acetic anhydride to give *acetyliminodiacetanilide*, m. p. 223—224°, and with absolute nitric acid to form *nitroiminodiacetotetranitroanilide*, $NO_2\cdot N[CH_2\cdot CO\cdot NH\cdot C_6H_3(NO_2)_2]_2$, which forms sulphur-yellow leaflets, m. p. 214—215° (decomp.), and dissolves in concentrated potassium hydroxide with blood-red colour. J. C. W.

The Diketopiperazines. VI. Action of Bromoacetamide on Glycineanilide. J. V. Dubsky and Ch. Gränacher (*Ber.*, 1917, **50**, 1701—1709).—Glycineanilide,

$$NH_2\cdot CH_2\cdot CO\cdot NHPh,2H_2O,$$

is conveniently prepared by saturating a solution of chloroacetanilide in alcohol (50 grams to 500 c.c.) with ammonia at a low temperature, heating the mixture in an autoclave at 50—60° for twelve to fifteen hours, and carefully concentrating the product. The yield is much poorer if smaller quantities are employed.

Bromoacetylglycineanilide, from bromoacetyl bromide and glycineanilide, forms slender needles, m. p. 170—172° (decomp.). It does not yield 2:5-diketo-1-phenylpiperazine when heated.

Reaction gradually sets in when equimolecular quantities of glycineanilide and bromoacetamide are mixed and left at 20°. The product is *triglycinediamideanilide*,

$$NHPh\cdot CO\cdot CH_2\cdot N(CH_2\cdot CO\cdot NH_2)_2,$$

which crystallises in stout platelets, m. p. 227° (decomp.), and is not soluble in organic media. The *hydrochloride*, m. p. 200—202°, is hydrolysed by water. When heated at 200—210°/vac., the compound loses ammonia and changes into 3:5-*diketopiperazine*-1-*acetanilide*, $NH{<}{\scriptstyle CO\cdot CH_2 \atop CO\cdot CH_2}{>}N\cdot CH_2\cdot CO\cdot NHPh$, which crystallises in glistening leaflets, m. p. 189—190°, and forms a readily dissociated *hydrochloride*, $1H_2O$, leaflets, and *nitrate*, $0{\cdot}5H_2O$, m. p. 124° (violent decomposition), whilst absolute nitric acid gives 3:5-*diketopiperazine*-1-op-*dinitroacetanilide*, very pale yellow needles, m. p. 225—226° (decomp.).

If the original glycineanilide contains iminodiacetanilide, which is usually the case, *triglycineamidedianilide*,

$$NH_2\cdot CO\cdot CH_2\cdot N(CH_2\cdot CO\cdot NHPh)_2,$$

is formed as well, in the reaction with bromoacetamide. This compound is freely soluble in alcohol, and so may be extracted from the product. It crystallises in long filaments, m. p. 165°. J. C. W.

Dyes of the Anthraquinone-2:1-acridone Series. Fritz Ullmann and Percy Dootson (*Ber.*, 1918, **51**, 9—24).—Ullmann and Billig have already described the influence on the tinctorial properties of anthraquinone-2:1-acridone exerted by sub-

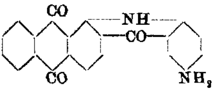
stituents in the half of the acridine system to which the anthraquinone residue is attached (A., 1911, i, 489, 490). The present communication is an outcome of an inquiry into the influence of substituents in the other part of the acridine system. The new derivatives are generally prepared by condensing 1-aminoanthraquinone with the methyl ester of a substituted *o*-chlorobenzoic acid, and then treating the corresponding free *o*-anthraquinonylaminobenzoic acid with concentrated sulphuric acid.

Methyl o-anthraquinonyl-1-*aminobenzoate* is prepared by boiling 1-aminoanthraquinone with methyl *o*-chlorobenzoate, potassium acetate, and a trace of copper acetate in naphthalene solution, the yield being 92%; it crystallises in red needles, m. p. 205° (corr.), is hydrolysed by alcoholic sodium hydroxide to the sodium salt, and is converted by warming with concentrated sulphuric acid, or with sodium hydroxide and hyposulphite at 40—50°, into anthraquinone-2:1-acridone. Similarly, 1:5-diaminoanthraquinone yields *dimethyl* o:o′-*anthraquinonyl*-1:5-*diaminodibenzoate*,

$$CO_2Me \cdot C_6H_4 \cdot NH \cdot C_6H_3 {<}^{CO}_{CO}{>} C_6H_3 \cdot NH \cdot C_6H_4 \cdot CO_2Me,$$

in brownish-violet, glistening crystals, m. p. 262° (corr., decomp.), which may be converted into the corresponding acid and di-acridone (*ibid.*).

Methyl 2-chloro-5-nitrobenzoate also condenses readily, giving an 87% yield of *methyl* 5′-*nitro*-2′-*anthraquinonyl*-1-*aminobenzoate*, which crystallises in blackish-red needles, m. p. 310° (corr.), and may be hydrolysed by *N*-sodium methoxide solution to the free *acid*, orange needles, m. p. 340°. This resists condensation to an acridone derivative, but the corresponding 5′-*amino*-2′-*anthraquinonyl*-1-*aminobenzoic acid*, which is obtained in dark violet crystals, m. p. 300° (decomp.), by reduction with sodium sulphide, may be condensed by fuming sulphuric acid (15% SO_3) to 2′-*amino-anthraquinone*-2:1-*acridone* (annexed formula). This crystallises in bluish-violet tablets, decomp. 340°, and dyes cotton in the vat the same shade, whereas the unsubstituted anthraquinoneacridone gives reddish-violet shades.

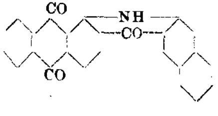


Methyl 2-chloro-5-methoxybenzoate does not react so rapidly, but gives *methyl* 2′-*anthraquinonyl*-1-*amino*-5′-*methoxybenzoate*, in the normal way. This crystallises in reddish-violet needles, m. p. 215° (corr.), whilst the free *acid* forms a felted mass of violet needles, m. p. 290° (decomp.), and may be converted into the chloride by boiling with phosphorus pentachloride and benzene, and then, by boiling with nitrobenzene, into 2′-*methoxyanthraquinone*-2:1-*acridone*. This forms small, violet leaflets, m. p. 308° (corr.), and gives a hyposulphite vat of the same colour.

For the preparation of the 3′-methoxy-compound, *p*-methoxy-anthranilic acid seemed to be the best starting material. This is synthesised as follows: *p*-toluidine is converted into 3-nitro-*p*-tolu-

idine sulphate, then into 2-nitro-*p*-cresol; this is methylated by means of methyl sulphate, and the ether is oxidised by boiling with permanganate solution to 2-nitro-4-methoxybenzoic acid, which is reduced by means of stannous chloride. 4-Methoxyanthranilic acid (see also Friedländer, A., 1912, i, 318) is boiled with 1-chloroanthraquinone, potassium carbonate, and copper acetate in amyl alcohol, and so converted into *2′-anthraquinonyl-1-amino-4′-methoxybenzoic acid*, which crystallises in violet needles, m. p. 272° (decomp.), and may be transformed, through its chloride, into *3′-methoxyanthraquinone-2 : 1-acridone*. This forms a wine-red mass of felted needles, m. p. 350° (corr.), gives a red vat, and dyes cotton red. The influence of the substituent in the para-position with regard to the carbonyl group is therefore of the same order as Friedländer observed in the case of indigotins and "thioindigos" (*loc. cit.*), and as has been found in the case of 3′-chloroanthraquinone-2 : 1-acridone (D.R.-P., 245875), namely, that the shade is modified in the direction of red.

Methyl 3-chloro-2-naphthoate, m. p. 58° (for the acid, see Strohbach, A., 1902, i, 149), condenses with 1-aminoanthraquinone to form *methyl 3′-anthraquinonyl-1-amino-2′-naphthoate*, violet needles, m. p. 277°, the corresponding *acid* crystallising in violet tablets, m. p. 322°. When the ester is shaken with alkaline sodium hyposulphite at 40—50° in the absence of air it gives a vat from which air precipitates *anthraquinone-2 : 1 : 2′ : 3′-naphthacridone* (annexed formula) (for the method, see D.R.-P., 246966). This crystallises in dark violet needles, m. p. 360°, and gives a green vat, from which cotton may be dyed bluish-violet. The isomeric 2 : 1 : 1′ : 2′-anthraquinonenaphthacridone of A., 1916, i, 484, and indanthrene-red B.N. extra, of D.R.-P., 237236, dye red shades. [See also *Ind.*, 178A.] J. C. W.



Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 298706, 1913; from *Chem. Zentr.*, 1917, ii, 347).—Iminazole compounds of the general formula $A\langle^{NR'}_{N}\rangle CR$, where *A* represents an anthraquinone group possibly containing other substituents, *R* an aryl or alkyl radicle, and *R′* an aryl radicle, can be obtained in good yield with simultaneous formation of water and halogen hydracid by treating *o*-halogen substituted acylaminoanthraquinones with primary aromatic amines in the presence of neutralising agents and catalysts, such as copper salts. The products are of value for the production of dyes.

3-*Bromo-1-N-phenyl-C-phenyl-1 : 2-anthraquinoneiminazole*, prepared by heating 1 : 3-dibromo-2-benzoylaminoanthraquinone with aniline, potassium acetate, and copper acetate, forms yellow needles, gives an orange-red solution in sulphuric acid, and on reduction

with hyposulphite gives a vat dyeing cotton pale yellow; by warming with fuming sulphuric acid it can be converted into a sulphonic acid. 1-N-p-*Tolyl*-C-*methyl*-1:2-*anthraquinoneiminazole*, yellow needles, m. p. 236°, obtained similarly from 1-chloro-2-acetylamino-anthraquinone and *p*-toluidine, gives a yellow solution in sulphuric acid and a hyposulphite vat which dyes wool yellow. D. F. T.

Chromoisomerism and Salt Formation of Iminovioluric Acids. I. I. LIFSCHITZ and LÉON KRITZMANN (*Ber.*, 1917, **50**, 1719—1738).—The bearing of residual affinity on questions of chromoisomerism and polychromism is now generally recognised, and therefore the study of a compound which can exist in tautomeric forms, and also give various internal salts by the exercise of subsidiary valencies, is of special interest. Such a compound is iminovioluric acid, which can exist, theoretically, in the following forms:—

$$CO<\begin{matrix}NH\text{——}CO\\NH\cdot C(NH)\end{matrix}>C:\overset{OH}{N} \qquad CO<\begin{matrix}NH\text{——}CO\\NH\cdot C(NH)\end{matrix}>C:\underset{OH}{N}$$

trans. *cis.*

$$CO<\begin{matrix}NH\cdot C(OH)\\NH\cdot C(NH)\end{matrix}>C\cdot NO \qquad CO<\begin{matrix}NH\text{——}CO\\NH\cdot C(NH_2)\end{matrix}>C\cdot NO$$

Nitroso-enol. Nitroso-amino.

The isomerism in the cases of the *cis*-modification and the nitroso-amino-form would be influenced by the possibility of internal salt formation.

Iminovioluric acid is an amphoteric substance, which forms colourless salts with mineral acids and pink or red salts with the alkalis and alkaline-earths. Spectrographically, the metallic salts are identical with those of the simple violurates, which indicates that the nitroso-group is modified and involved in the establishment of a "residual affinity ring." The salts with mineral acids are optically identical with violuric acid itself, and therefore contain no residual affinity rings. The silver salt exists in a pink and a bluish-violet form, the former being most probably a salt of the above *trans*-modification, with the metallic atom linked by residual affinity to the carbonyl group, whilst the latter may be derived from the *cis*-acid, with a subsidiary valency uniting the metal and the imino-group.

The free iminovioluric acid has been isolated in three forms. The commonest is red, and spectrographically like its alkali salts; that is, it is the internally-complex form of the *cis*-modification. Another is yellowish-orange, and is to be regarded as the *trans*-isomeride, whilst the third is blue, and is most probably an internally-complex form of the nitroso-amino-type.

Some salts of iminovioluric acid were prepared by Traube in his synthesis of uric acid (A., 1900, i, 416), but the following scheme

represents an improved method: $CO(NH_2)_2 + CN{\cdot}CH_2{\cdot}CO_2H$ (with Ac_2O) $\longrightarrow NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$. This

$$+ NaOH \longrightarrow CO{<}\begin{matrix}NH\text{——}CO\\NH{\cdot}C(NH)\end{matrix}{>}CH_2$$

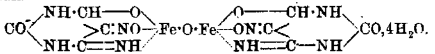
and this $+ NaNO_2 + HCl \longrightarrow$ sodium hydrogen salt of iminovioluric acid, or the normal salt, according to the conditions of the reaction.

Sodium iminoviolurate, $C_4H_3O_3N_4Na$, crystallises in silky, pink threads, and the acid salt, $C_8H_7O_6N_8Na,2{\cdot}5H_2O$, is reddish-violet. The *potassium* salts, obtained by similar methods, using potassium nitrite, are also pink and reddish-violet, but the acid salt has only $1H_2O$. From the sodium salt the following new salts have been prepared: *magnesium*, $MgX_2,6H_2O$, a yellow, microcrystalline powder, and MgX_2, a bright brick-red powder; *barium*, BaX_2,H_2O, red, and $Ba_3X_2,5H_2O$, pale pink; *cupric*, $CuX_2,2H_2O$, pale green, and CuX_2, almost black; *silver*, AgX,H_2O, pink, AgX, bluish-violet, and Ag_3X,xH_2O, yellow; *strychnine*, blue; *brucine*, $BX,2{\cdot}5H_2O$, yellow, BX, red, $BX,1{\cdot}5H_2O$, blue; *sulphate*, $(C_4H_4O_3N_4)_2,H_2SO_4$, colourless, m. p. 140° (loss of water); *hydrochloride*, $C_4H_4O_3N_4,HCl,H_2O$, unstable in the air. For the details of the conditions under which the various salts are formed, the original should be consulted.

Two *dimethyl* esters have also been obtained by treating the sodium salt with methyl sulphate; one is pale yellow and gives a yellow solution in sodium hydroxide, the other is orange-yellow and gives a red solution. Different ethyl esters are also formed when the different silver salts are treated with ethyl iodide.

The three forms of the free *iminovioluric acid* are obtained thus: *yellowish-orange*, by covering the sodium salt with 2- to 3-*N*-mineral acids; violet-tinted *red*, by exactly neutralising the sodium salt; *bluish-violet*, by boiling the others with water.

If the sodium salt is reduced with ferrous sulphate, or the free acid with iron, a very dark blue solution is obtained. In concentrated solutions, the new product may be obtained as a precipitate, which is a dark blue powder with coppery lustre. The *compound* gives a colourless solution in dilute acetic acid, from which it may be precipitated again by alkalis, and it may be represented by the formula

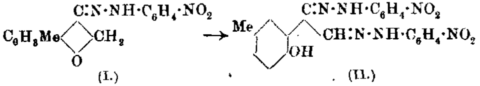


J. C. W.

Various Observations on Phenylhydrazones, Semicarbazones, and Anils. K. von Auwers (*Ber.*, 1917, **50**, 1585—1614. Compare this vol., i, 27).

A. Phenylhydrazones.—Equimolecular proportions of 4-methylcoumaran-2-one and *p*-nitrophenylhydrazine hydrochloride react in aqueous-alcoholic solutions in the cold to form the normal p-*nitrophenylhydrazone* (I), which crystallises in red leaflets with metallic

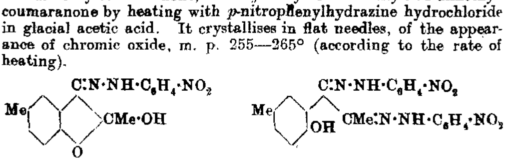
green reflex, m. p. 200—204°. With an excess of the basic reagent, in boiling solutions, the coumaranone ring is opened, and the *di*-p-*nitrophenylhydrazone* of 4-*hydroxy*-m-*tolylglyoxal* (II) is formed, in dark reddish-violet leaflets, m. p. 276°.



(I.) (II.)

1:4-Dimethylcoumaran-2-one and *p*-bromophenylhydrazine combine without the elimination of water, the product being most probably the p-*bromophenylhydrazone* of 1-*hydroxy*-1:4-*dimethylcoumaran*-2-*one*, since it is a pale yellow powder which is not soluble in sodium hydroxide. With 1-ethoxy-1:4-dimethylcoumaranone and the same base in boiling alcohol, rupture of the ring takes place to a certain extent, for the *di*-p-*bromophenylhydrazone* of 4-*hydroxy*-m-*tolyl methyl diketone*, pale yellow, flat needles, m. p. 148—149°, is formed as a by-product (compare formula II or IV).

The reaction between 1:4-dimethylcoumaran-2-one and *p*-nitrophenylhydrazine is somewhat complicated. In the main, the ring is opened and an osazone is formed, but the mother liquors from this contain the p-*nitrophenylhydrazone* of 1-*hydroxy*-1:4-*dimethylcoumaran*-2-*one* (III), which forms rosettes of orange-yellow needles, m. p. 171—172°. The osazone, 4-*hydroxy*-m-*tolyl methyl diketone di*-p-*nitrophenylhydrazone*, (IV), is produced from 1:4-dimethylcoumaranone, or 1-hydroxy- or 1-ethoxy-1:4-dimethylcoumaranone by heating with *p*-nitrophenylhydrazine hydrochloride in glacial acetic acid. It crystallises in flat needles, of the appearance of chromic oxide, m. p. 255—265° (according to the rate of heating).



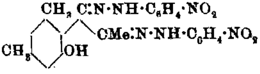
(III.) (IV.)

If a solution of this osazone in acetone is diluted with water or allowed to evaporate, a salmon-coloured precipitate, which looks like clean copper in the mass, is formed. This is a "*hydrate*," the elements of water being attached at one of the –C:N– groups; it has m. p. 273—274°, and loses water again if boiled with aromatic hydrocarbons or glacial acetic acid, but not by heating alone at 130°. A different "*hydrate*" is formed if the reaction between 1:4-dimethylcoumaranone and *p*-nitrophenylhydrazine is carried out in cold or boiling alcohol, or if 1-hydroxy-1:4-dimethylcoumaranone is treated with the base in boiling alcohol; this isomeride is of a bright brick-red colour, has m. p. 265—270°, and may be dehydrated more readily. A pale brick-red "*dihydrate*"

is also formed from 1-hydroxy-1:4-dimethylcoumaranone in the cold.

The colour and stability of these "hydrates" seem to depend considerably on the mode of preparation. From the analytical data, it appears that the osazone has a tendency to hold water and aromatic hydrocarbons more or less firmly, not only in chemical but also in mechanical union. It is remarkable that, of all the coumaranones, only the 1:4-dimethyl- (and 1-hydroxy-1:4-dimethyl-) componnd yields these hydrates of osazones. 1-Hydroxy-1:4-dimethylcoumaran-2-one can also be converted into a normal p-*bromophenylhydrazone*, golden-yellow prisms or brilliant, sulphur-yellow needles,, m. p. 149°, and a normal p-*nitrophenylhydrazone*, slender, sulphnr-yellow needles or amber-coloured, stout prisms, m. p. 176—177°.

In other cases, normal hydrazones are formed or osazones, after opening of the ring, but it frequently happens that the latter are dimorphic. Thus, 4-methyl-1-ethylcoumaran-2-one gives the *di*-p-*nitrophenylhydrazone* of *4-hydroxy*-m-*tolyl ethyl diketone*, in orange-red needles, with blue reflex, m. p. 248—249°; occasionally, chromic oxide coloured leaflets or flat needles, possibly a "hydrate," were obtained. 4-Methyl-1-*iso*propylcoumaranone yields the *di*-p-*nitrophenylhydrazone* of *4-hydroxy*-m-*tolyl* iso*propyl diketone*; deep orange-red crystals from much methyl alcohol, and stout, yellow prisms from glacial acetic acid, m. p. 254—255°. The difference in colour between the osazones of the ethyl and *iso*propyl tolyl diketones is remarkable. 1:3:5-Trimethylcoumaran-2-one forms a normal p-*nitrophenylhydrazone*, in orange-red needles and scales, m. p. 214—215°, when treated with the base in cold alcohol, and the di-*p*-nitrophenylhydrazone of *5-hydroxy*-m-*xylyl-4-methyl diketone* (annexed formula), deep ruby-red needles, m. p. 281°, in hot solutions.



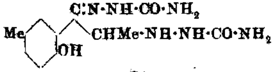
The *p*-nitrophenylhydrazone of benzaldehyde yields an *acetyl derivative*,

$$CHPh{:}N{\cdot}NAc{\cdot}C_6H_4{\cdot}NO_2,$$

small, pale yellow needles, m. p. 174—175°, when treated with acetyl chloride, and the *triacetate*, $OAc{\cdot}CHPh{\cdot}NAc{\cdot}NAc{\cdot}C_6H_4{\cdot}NO_2$, colourless scales, m. p. 154—155°, when warmed with acetic anhydride and a trace of concentrated sulphuric acid.

B. Semicarbazones.—In this section, some cases of "hydrates" of semicarbazones are described.

1:4-Dimethylcoumaran-2-one suffers rupture of the ring when warmed with semicarbazide at 40—50°, the product being *4-hydroxy*-m-*tolyl α-semicarbazidoethyl ketone semicarbazone* (I),



(I.)

$$\begin{array}{l}C_6H_3Me{\cdot}OH \\ | \\ C(OH){\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 \\ | \\ CHMe{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2\end{array}$$

(II.)

m. p. 227°. This is precipitated as a "*hydrate*" (II), m. p. 227°, if its alkaline solutions are acidified.

1-Hydroxy-1 : 4-dimethylcoumaranone yields products, m. p. 207—210° and 227—228°, which give analytical results between the values for the true disemicarbazone of 4-hydroxy-*m*-tolyl methyl diketone and its monohydrate. 4-Methyl-1-ethylcoumaranone gives *4-hydroxy-*m*-tolyl α-semicarbazidopropyl ketone semicarbazone*, glassy, flat needles and rhombic plates, m. p. 230° (quickly heated; compare also this vol., i, 29), and its "*hydrate*," m. p. 160°. Phenyl methyl diketone forms a normal *disemicarbazone*, m. p. 229—232°.

C. Anils.—Whilst anils show little tendency to combine with water to form "hydrates" of the type OH·CHR·NHR′, they do sometimes unite with acetic acid to form compounds of the type OH·CHR·NAcR′. Some new examples are now given.

5-Nitrosalicylaldehyde yields *5-nitrosalicylideneaniline*, yellow needles, m. p. 133°, which reacts with boiling acetic anhydride to form the *compound*,

$$OAc\cdot C_6H_3(NO_2)\cdot CH(OH)\cdot NPhAc,$$

colourless needles, m. p. 145°. *5-Nitro-4-hydroxy-*m*-tolylideneaniline*, orange-red, flat needles, m. p. 133·5—134·5°, forms an *aniline* salt, stout, ruby-red prisms, and reacts with acetic anhydride to give the *compound*, $OAc\cdot C_6H_2Me(NO_2)\cdot CH(OH)\cdot NPhAc$, white platelets, m. p. 167°. *5-Nitro-2-hydroxy-*m*-tolylideneaniline*, golden-yellow needles, m. p. 176—177°, forms a *diacetate*, isomeric with the last, in glistening scales, m. p. 153—154°. J. C. W.

Diaryl-substituted Hydrazidinecarboxylic Esters and their Hydrolytic Products. Degradation of Ethyl Acetoacetate to Derivatives of Formic Acid. Carl Bülow and Richard Huss (*Ber.*, 1918, **51**, 24—42).—The hydrolytic degradation, and other reactions, of the hydrazidinecarboxylates derived from ethyl acetoacetate (this vol., i, 42) have been studied in order to confirm the constitution assigned to them. Ethyl α-*o*-toluidinoglyoxylate 2 : 4-dichlorophenylhydrazone,

$$C_6H_3Cl_2\cdot NH\cdot N:C(NH\cdot C_6H_4Me)\cdot CO_2Et,$$

has been chosen for the purpose, as the possible products offer few difficulties in the way of identifying them.

I. *Proof of the Carbethoxyl Group.*—The ester is converted by contact with alcoholic ammonia into *α-o-toluidinoglyoxylamide 2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N:C(NH\cdot C_6H_4Me)\cdot CO\cdot NH_2,$$

which crystallises in small needles, m. p. 152°, dissolves without change in concentrated sulphuric acid, and changes into a golden-yellow solid, with evolution of gas, if heated above its m. p. The same amide may be formed by melting the 2 : 4-dichlorophenylhydrazone of α-chloroglyoxylamide (A., 1913, i, 911) with *o*-toluidine.

The ester may also be converted into the *2 : 4-dichlorophenylhydrazone* of *α-o-toluidinoglyoxylhydrazide*,

$$C_6H_3Cl_2\cdot NH\cdot N:C(NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot NH_2$$

which crystallises in prisms, m. p. 145°, and condenses with aldehydes and ketones in the normal way. The *isopropylidene* compound, $C_6H_3Cl_2\cdot NH\cdot N\colon C(NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot N\colon CMe_2$, from acetone, forms slender needles, m. p. 202°, and reacts with chlorine in cold alcoholic suspension to give 2:4-dichlorophenyldiazonium chloride, which later on suffers decomposition in some inexplicable manner. The *benzylidene* compound crystallises in glistening needles, m. p. 176°, and also gives 2:4-dichlorophenyldiazonium chloride when treated with chlorine, the product yielding a crystalline, yellowish-red dye with β-naphthol. The *o-chlorobenzylidene* compound has m. p. 198°, and apparently does not give a diazonium salt if treated with chlorine in ethereal suspension. The *salicylidene* compound forms glistening, yellow needles, m. p. 186°, and is not attacked by chlorine in light petroleum. The *m-nitrobenzylidene* compound forms glistening, pale golden-yellow needles, m. p. 229°. Ethyl diacetylsuccinate also condenses with the hydrazide, giving the 2:4-*dichlorophenylhydrazone* of *ethyl* 1-α-o-*toluidinoglyoxylamido*-2:5-*dimethylpyrrole*-3:4-*dicarboxylate*,

$$\begin{matrix} C_6H_3Cl\cdot NH\cdot N \\ C_6H_4Me\cdot NH \end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot N\!<\!\!\begin{matrix} CMe\colon C\cdot CO_2Et \\ CMe\colon C\cdot CO_2Et \end{matrix}$$

in white needles, m. p. 225°, which yields a diazonium salt with chlorine.

II. *Action of Acetic Anhydride.*—The compound readily yields an *acetyl* derivative, $C_{19}H_{19}O_3N_3Cl_2$, in colourless plates, m. p. 115°, which is also converted into a diazonium salt by chlorine.

III. *Degradation to the Hydrazidine of Formic Acid.*—The ester is wetted with alcohol and warmed with 20% potassium hydroxide at 95° for a few minutes, when a new potassium salt separates, which is dissolved in warm water and mixed with hydrochloric acid. Free *a-toluidinoglyoxylic acid* 2:4-*dichlorophenylhydrazone* separates as a lemon-yellow mass, which becomes dark brown in time, even in a well-closed bottle, and gives golden-yellow solutions in most solvents. It has m. p. 98°, but if kept at this temperature in an evacuated vessel, it soon loses carbon dioxide and changes into o-*toluidinoformaldehyde* 2:4-*dichlorophenylhydrazone*,

$$C_6H_4Me\cdot NH\cdot CH\colon N\cdot NH\cdot C_6H_3Cl_2,$$

which forms white needles, m. p. 91°.

IV. *Complete Disruption.*—The ester is decomposed by warming with zinc dust and glacial acetic acid into 2:4-dichloroaniline and *o*-toluidine, this being identified by removing the solid base as far as possible and converting the oil into *o*-tolueneazo-β-naphthol. The ester may be recovered almost entirely unchanged after boiling with water for a week, but it is hydrolysed by boiling hydrochloric acid, yielding 2:4-dichlorophenylhydrazine, m. p. 90°, oxalic acid, and *o*-toluidine. J. C. W.

Hydrazides and Azides of Sulphocarboxylic Acids. ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], **96**, 180—185).—When hydrazine and *o*-cyanobenzenesulphonyl chloride react in benzene solution, the product is a heterocyclic compound, *o-sulphohydrazido-*

benzohydrazide anhydride, $SO_2<\genfrac{}{}{0pt}{}{NH\cdot N}{C_6H_4-}>C\cdot NH\cdot NH_2$, needles, m. p. 154° (decomp.), which with benzaldehyde yields a *benzylidene* derivative, $C_{14}H_{12}O_2N_4S$, prisms, m. p. 179°. With aqueous sodium azide, an ethereal solution of *o*-cyanobenzenesulphonyl chloride slowly reacts with formation of o-*cyanobenzenesulphonylazide*, $CN\cdot C_6H_4\cdot SO_2\cdot N_3$, non-explosive rhombohedra, m. p. 40°.

D. F. T.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. VI. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1917, **101**, 15—24. Compare A., 1917, i, 711).—The ethereal extract of the products of the action of nitric acid on proteins yields, on fractional crystallisation from hot water, benzoic and *m*-nitrobenzoic acids, both of which are probably formed from the aromatic amino-acids in the protein.

From the aqueous extract of the precipitate formed by the addition of barium hydroxide and alcohol to the hydrolysed protein solution (compare A., 1915, i, 324), shining, yellow prisms separate after some days, from which, on treatment with dilute nitric acid, an *acid substance*, $C_4H_3O_4N_3$, is liberated which melts at about 300°. It appears to be a derivative of glyoxaline.

During the extraction of the products of the action of nitric acid on hæmoglobin by ether, a yellow powder gradually settles out from the originally clear liquid. On recrystallisation, an *acid substance* is obtained in small, colourless, polygonal crystals, $C_5H_3O_3N_2$, m. p. about 300°.

Among the products of the combined action of hydrochloric and nitric acids on gluten, a substance was isolated which crystallised in slender needles, but appeared, nevertheless, to be a mixture of chlorinated benzoic acids.

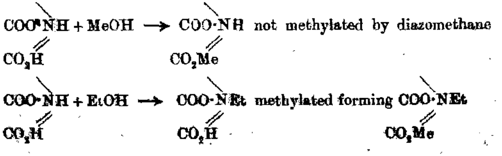
H. W. B.

Effects of Electrolytes on Gelatin and their Biological Significance. I. Effects of Acids and Salts on the Precipitation of Gelatin by Alcohol. W. O. FENN (*J. Biol. Chem.*, 1918, **33**, 279—294).—The author finds that the quantity of alcohol required to precipitate a fixed amount of gelatin from its solution is dependent on the nature and number of ions present in the gelatin solution. The method consists essentially in adding 95% alcohol to 5 c.c. of the gelatin–electrolyte mixture in a test-tube until such an opacity is produced that a pencil held behind the test-tube can no longer be seen. The number of c.c. of alcohol added constitutes the "alcohol number."

The results show that acids, alkalis, and salts hinder the precipitation of gelatin by alcohol. In the case of strong acids and alkalis, this effect rapidly increases, passes through a sharp maximum, and then decreases as the concentration of the electrolyte is increased. Thus, when the conditions above described are observed, the quantity of alcohol required to precipitate the gelatin rapidly increases as the concentration of hydrochloric acid in the gelatin solution is raised from 0 to 0·024*M*. From 0·024 to 0·095*M*, precipitation does not occur, however much alcohol is added, whilst

beyond this limit the amount of alcohol required slowly diminishes. When salts are added, the precipitation of the gelatin is also hindered, and the effect becomes more marked as the concentration of the salt is increased. Tervalent ions are more effective than bivalent, and bivalent than univalent in this respect. Certain salts, such as aluminium and copper chlorides, which are very effective in hindering precipitation by alcohol, resemble the strong *acids in that their effect passes through a maximum and then* decreases. Others, such as manganese sulphate, containing bivalent cations and anions, are exceptions to the general rule, and either assist or only very slightly hinder the precipitation of gelatin by alcohol. The effect of the sulphates, citrates, and tartrates of the alkali metals decreases in high concentrations, due to their strong "salting out" or dehydrating powers. Eventually a point is reached where the salt *itself* precipitates the gelatin without any addition of alcohol being required. The discussion of the theoretical significance of these results is reserved for a future communication. H. W. B.

Action of Diazomethane on Hæmin. WILLIAM KÜSTER [with OTTO GEERING and O. KUSCH] (*Zeitsch. physiol. Chem.*, 1917, **101**, 25—32. Compare A., 1915, i, 853).—It has been stated (*loc. cit.*) that whereas bilirubin and hæmatoporphyrin are readily esterified by diazomethane, hæmin is only esterified with difficulty or not at all. Further experiments have shown that only a very small percentage of α-chlorohæmin is esterified by diazomethane, whilst α-bromohæmin is quite unattacked. On the other hand, some β-hæmin derivatives have been found to be readily methylated by this *reagent*. *β-Bromoethylhæmin* is *converted* into *β-methyl*ethylhæmin and β-chlorohæmin into β-chloromethylhæmin; but β-chloromethylhæmin is unattacked, and in mixtures containing β-chlorohæmin and the methyl mono-ester, only the β-chlorohæmin undergoes methylation. The methylation of the second carboxyl in β-hæmin can therefore only occur through the agency of diazomethane when the first carboxyl has been esterified by the ethyl *radicle, and hence it follows that the carboxyl esterified* by ethyl alcohol is different from that esterified by methyl alcohol. These results furnish new evidence for the view that the carboxyl radicles in hæmin are affected in different ways by the neighbouring basic and iron-containing groups (compare A., 1912, i, 670), one being in closer relation to the basic group than the other. This is illustrated by the scheme:



β-Bromoethylhaemin, $C_{36}H_{36}O_4N_4BrFe$, prepared by Mörner's method, when suspended in chloroform and treated with diazomethane, yields *β-bromomethylethylhaemin*, $C_{37}H_{38}O_4N_4BrFe$, which is insoluble in 5% sodium carbonate solution. H. W. B.

Esterification and Empirical Composition of Hæmin. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1917, **101**, 33—42. Compare preceding abstract).—Hæmin prepared by Mörner's method, using pure ethyl alcohol, consists of a mixture of *α*-hæmin and monoethylhæmin, whilst when methyl alcohol is employed, the products consist of *β*-hæmin, monomethyl-, and dimethyl-hæmin. When a mixture of ethyl and methyl alcohols is used, methylhæmin is first formed, which then interacts with the ethyl alcohol to form ethylhæmin. Since it has been shown (*loc. cit.*) that ethyl and methyl alcohols become attached to different carboxyl groups, it follows that the ethylhæmin formed by the direct action of ethyl alcohol on hæmin should be isomeric with that formed by the action of the mixture of alcohols in which the ethylhæmin is produced from the primary methylhæmin. Experiments carried out on these lines have not been so far successful in isolating two isomeric ethylhæmins, only mixtures of mono- and dialkyl-hæmins being obtained.

The analyses of the alkyl- and halogen-hæmins prepared in various ways are all in harmony with the empirical formula $C_{34}H_{32}O_4N_4Cl(Br)Fe$ for hæmin. H. W. B.

Action of Aniline on Hæmin and its Transformation by the Acetic Acid Method. WILLIAM KÜSTER [with, in part, LOBMILLER] (*Zeitsch. physiol. Chem.*, 1917, **101**, 43—76. Compare A., 1914, i, 887, and preceding abstracts).—The product of the action of aniline on hæmin consists of a mixture of three substances. One of these, hydroxyhæmin, is formed from chloro- or bromo-hæmin by the probable intermediate production of an additive compound of the hæmin with aniline, which subsequently undergoes hydrolysis. It acts as a base, forming salts with acids, and has the hydroxyl group attached directly to the iron atom in the hæmin molecule. The other two products are two dehydrohalogenohæmins, in one of which the iron atom is attached to oxygen and in the other to nitrogen. The latter *N*-derivative is more stable than the *O*-derivative, and therefore does not so readily undergo transformation into a true hæmin. By the action of aniline on *β*-chloromethylhæmin, *N*-dehydrochlorohæmin and hydroxyhæmin are formed, of which only the latter yields crystalline *β*-dimethylhæmin when esterified by means of methyl alcohol and hydrogen chloride.

Two *α*-dehydrobromohæmins are similarly produced by the action of aniline on *α*-bromohæmin, and can be separated by treating with a pyridine–chloroform mixture. Part dissolves, but the solution does not yield hæmin when poured into acetic acid containing sodium chloride. The insoluble portion dissolves in alcoholic ammonia, and is readily converted into crystallised hæmin. In the first case, the iron atom is attached to nitrogen, whilst in the

second the less stable iron–oxygen compound is present, which is therefore transformable into hæmin.

In some cases, the failure to re-form a crystalline hæmin from a methylated hæmin is ascribed to the intermediate production of a "pseudohæmin," in which salt formation with one of the basic *nitrogen atoms is assumed to occur.* H. W. B.

The Influence of Neutral Salts on the Action of Urease. J. TEMMINCK GROLL (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 559—565).—The cations exert a preponderating influence on the decomposition of carbamide by urease, the anions having comparatively little influence. The cations and the anions, in so far as the influence of the latter can be observed, arrange themselves, as regards their retarding action on urease, in much the same order as they do in regard to their influence on various colloidal phenomena. W. G.

Physiological Chemistry.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. I. High Levels of Carbon Dioxide and Alkali. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 333—344).—The authors describe experiments on dogs which show that when, by means of subcutaneous injections of *morphine, respiration is depressed and the alveolar carbon dioxide* is raised, or when, by the administration of carbon dioxide in the air breathed, the carbon dioxide content of the blood is raised above the normal level, the "carbon dioxide capacity" or "alkaline reserve" (Van Slyke and Cullen, A., 1917, i, 521) of the blood also rises. This rise is probably due to a compensatory passage of alkali from the tissues into the blood. Through this mechanism, *respiration exerts a powerful influence on the* alkaline reserve of the blood. H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. II. Low Levels of Carbon Dioxide and Alkali induced by Ether. Their Prevention and Reversal. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 345—353. Compare preceding abstract).—The disturbance of the alkaline reserve or (as the authors prefer to call it) the carbon dioxide capacity of the blood by administration of ether appears from these experiments to be wholly dependent on disturbance of respiration. If the anæsthesia is managed so that respiration is but little increased, the lowering of the alkaline reserve of the blood is slight. When, however, respiration is simultaneously

excited, the alkaline reserve may be greatly reduced. Down to a certain critical level, recovery may spontaneously ensue, but below this level the changes appear to become irreversible, resulting in the death of the animal. Light anæsthesia loses its harmful tendencies when sufficient carbon dioxide is administered to maintain the alveolar carbon dioxide at the normal level. It follows that, in ether anæsthesia, the alkaline reserve or carbon dioxide capacity of the blood is determined and controlled by its carbon dioxide content, which is in turn dependent on the alveolar carbon dioxide, or eventually on the respiration.

When the ether anæsthesia is so profound as to depress respiration, a rise occurs in the alkaline reserve of the blood.

H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. III. The Effects of Excessive Pulmonary Ventilation. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 355—363. Compare preceding abstracts).—The authors describe experiments on dogs which show that excessive pulmonary ventilation by means of artificial respiration induces not only a lowering of the carbon dioxide content, but also of the alkaline reserve of the blood. The arterial pressure also falls, and death may follow. If the artificial respiration, instead of being made with fresh air, is carried on by continual reinjection mainly of expired air, so that the carbon dioxide content of the blood is not reduced, the alkaline reserve and arterial pressure do not fall and the other ill-effects also fail to appear. H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. IV. The Sequence of Trauma, Excessive Breathing, Reduced Carbon Dioxide Capacity, and Shock. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 365—371. Compare preceding abstracts).—The experiments show that trauma does not cause a lowering of the carbon dioxide capacity or alkaline reserve of the blood if measures are taken to prevent excessive pulmonary ventilation. Beneficial results may therefore be expected to attend the administration of carbon dioxide to wounded soldiers with the view of the prevention of "shock."

H. W. B.

The Occurrence of Creatine and Creatinine in the Blood in Normal and Pathological Conditions. II. In Young Individuals: Method of Estimation. JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **84**, 264—280).—The creatinine content of blood in children up to fifteen years of age is smaller than is that of adult men. The author confirms the value of Folin's method for estimating creatinine, especially the modification of Folin and Doisy, and rejects the unfavourable criticisms of MacCrudden and Sargent. Attention is directed to the necessity of employing pure reagents. S. B. S.

The Physical Chemistry of the White Corpuscles and Pus. F. TANGL and K. BODON (*Biochem. Zeitsch.*, 1917, **84**, 183—193). —Measurements of the electrical conductivity of the whole pus, serum, and leucocytes. The conductivity of the last-named is least. If these are diluted with water, the conductivity diminishes progressively with the dilution, and in this respect they differ from erythrocytes, of which the conductivity progressively increases on dilution up to a certain point, beyond which further addition of water causes a diminution of conductivity. S. B. S.

Phosphates in Human Blood-serum. IV. Orthophosphates and Residual Phosphorus in Bright's Disease. JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **84**, 231—245).—Attention is directed to the differences in the distribution of phosphorus in the serum in cases of typical (acute) and chronic glomerular *nephritis*. S. B. S.

The Change in the Hydrion Concentration of Muscle during Work. J. GOLDBERGER (*Biochem. Zeitsch.*, 1917, **84**, 201—209).—The reaction of extracts of muscular tissue (gastrocnemius of frogs) is always slightly acid when determined electrometrically. The hydrion concentration increases after muscular work. The acidity, determined by titration (to phenolphthalein), is seven to ten thousand times greater than that determined electrometrically. The increased acidity due to muscular work is caused chiefly by volatile acids, chiefly carbon dioxide. S. B. S.

The Reaction of Human Milk. ALEXANDER SZILI (*Biochem. Zeitsch.*, 1917, **84**, 194—200).—The hydrion concentration of milk is almost exactly that of water when measured electrometrically, and does not change appreciably during the course of lactation. The milk in the later stages of lactation requires somewhat less alkali than in the earlier stages for neutralisation to phenolphthalein. S. B. S.

New Constituents of Milk. III. A New Protein, Soluble in Alcohol. THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*, 1918, **33**, 243—251. Compare A., 1917, i, 103).—The new protein is precipitated, together with caseinogen, when dilute hydrochloric acid is added to milk. The precipitated proteins are purified by repeatedly dissolving in dilnte alkali and reprecipitating with dilute acetic or hydrochloric acid. The moist proteins are now treated with an equal volume of 92% alcohol; the new protein dissolves, and on pouring the concentrated filtrate into water, it separates in flocculent masses, which can be collected on a filter, washed, and dried over sulphuric acid. The white powder finally obtained gives the following figures: 54·91% C, 7·17% H, 15·71% N, 0·95% S, and 0·08% P. It thus contains more carbon and sulphur and less phosphorus than caseinogen. When examined by Haus

mann's method for the distribution of nitrogen, the new protein does not yield more amide-N or less basic-N than do caseinogen and other animal proteins, and in this respect does not resemble the alcohol-soluble proteins of vegetable origin, although so like gliadin in its solubility in relatively strong alcohol. That it is quite distinct from all the other proteins in milk is shown not only by its behaviour towards solvents and its chemical composition, but also by the fact that it does not react anaphylactically with any of these other proteins, although it is itself highly anaphylactogenic.

The alcohol-soluble milk protein possesses distinctly acid properties; it is almost insoluble in water, but dissolves in dilute alkalis. The solubility of the protein in alcohol of various degrees of concentration depends much on the temperature; it dissolves readily in warm 70% alcohol, but a small proportion separates out on cooling. It is insoluble in absolute alcohol.

Although the new protein is precipitated from its solutions by acids, it is nevertheless completely dissolved by very dilute acetic acid. On adding potassium ferrocyanide, a voluminous precipitate is produced. The protein also gives strong tryptophan, Millon's and biuret reactions. These properties distinguish it from any type of protein hitherto discovered in animal tissues or products.

H. W. B.

Mathematical Formulæ and Acid Excretion. GEORGE D. BARNETT (*J. Biol. Chem.*, 1918, **33**, 267—270. Compare Fitz and Van Slyke, A., 1917, i, 522).—The author raises a protest against the introduction of complex mathematical formulæ to express the relations existing between the various factors concerned in the excretion of urine by the kidney. It is shown that the results obtained by Fitz and Van Slyke, which were stated to be in agreement with the modification of Ambard's formula, plasma carbon dioxide $= 80 - \sqrt{D/W} \cdot \sqrt{C}$, can be even better expressed by the simpler formula, plasma carbon dioxide $= 80 - 5\sqrt{D/W}$. Other formulæ are also put forward which express the relations between the results with a greater degree of accuracy than is attained by Fitz and Van Slyke's formula. Moreover, it is pointed out that using Fitz and Van Slyke's formula, the average deviation of "calculated" from "found" values of plasma carbon dioxide is much greater than would result if maximal additive errors occurred in all the estimations involved.

H. W. B.

Acidosis. X. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **33**, 271—278. Compare preceding abstract).—The author agrees that the simplified formula, plasma carbon dioxide $= 80 - 5\sqrt{D/W}$, put forward by Barnett (*loc. cit.*) expresses with the greatest degree of accuracy the relationship existing between alkaline reserve and acid excretion. The additional formulæ advanced by Barnett are shown to fail when applied in the cases of children.

H. W. B.

Physico-chemical Investigations on Experimental Uræmia. M. Bienenstock and L. Csáki (*Biochem. Zeitsch.*, 1917, **84**, 210—224).—Dogs were rendered uræmic either by extirpation of the kidneys or by ligaturing the ureters. The following constants of the serum were determined before and after operation: dry matter, ash (soluble and insoluble in water), organic matter, surface tension, refraction, viscosity, lowering of freezing point, conductivity, hydrion concentration, nitrogen, number and volume of red corpuscles. The animals were allowed food and water after the operations, and the changes produced by the uræmia were not always in the same direction. The general results seem to warrant the conclusion, however, that uræmia causes an increase of the organic molecules in the serum and a diminution of the inorganic; the increase of the former is larger than the diminution of the latter, so that the total number of the molecules is increased. The fact of the diminution of the inorganic molecules was confirmed by estimation of chlorine in the serum of animals which had been deprived of food and water after the operation. The results are ascribed generally to the increase of the acidity of the serum produced by uræmia. S. B. S.

Pyruvic Acid. L. Karczag (*Biochem. Zeitsch.*, 1917, **84**, 225—230).—Both rats and guinea-pigs show a high tolerance to the acid. The injection produces neither hyperglycæmia, nor excretion in the urine of dextrose, lactic acid, volatile fatty acids, or pyruvic acid. The urine excreted is alkaline and contains a large amount of carbonate.

Certain bacteria bring about the fermentation of pyruvic acid only when grown on bouillon, but not on simpler media.

S. B. S.

Metabolic Changes induced by Administration of Guanidine Bases. I. Influence of Injected Guanidine Hydrochloride on the Sugar Content of the Blood. C. K. Watanabe (*J. Biol. Chem.*, 1918, **33**, 253—265).—The injection of guanidine hydrochloride into a rabbit is followed by symptoms which are almost identical with those of tetanus produced by extirpation of the parathyroid glands. It is now shown that hypoglycæmia results from the injection of guanidine hydrochloride, and since guanidine derivatives are known to appear in considerable amounts in the blood and urine after parathyroidectomy (Koch, A., 1913, i, 935), it is probable that the hypoglycæmia observed after the experimental removal of the parathyroids in animals (Underhill and Blatherwick, A., 1917, i, 897) or in tetanus in man is a secondary effect produced by guanidine poisoning. H. W. B.

Methods of Gas Warfare. S. J. M. Auld (*J. Washington Acad. Sci.*, 1918, **8**, 45—58).—A popular chronological account of the methods used by the Germans in gas attack. The first attack

was made by chlorine in the form of a gas cloud, this being followed by the use of phosgene [carbonyl chloride]. In gas shells, various substances were used. The original "tear" shells contained almost pure xylyl bromide or benzyl bromide, but some of the shells were rendered almost inactive by the presence of 20% of the dibromide. Later, chloromethyl and trichloromethyl chloroformates were used. They had no decided reaction on the eyes, but were highly poisonous. One of the latest substances used was dichlorodiethyl sulphide (mustard gas), which acted as a "superlachrymator." It had no immediate action on the eyes beyond causing slight irritation, but after several hours the eyes began to swell and inflame and practically to blister, the nose discharged freely, and severe coughing and even vomiting ensued. Direct contact with the spray caused severe blistering of the skin. Other substances used were: (1) in shells, allylthiocarbimide, bromomethyl ethyl ketone, methyl bromoethyl ketone, methyl dibromoethyl ketone, $CH_3\cdot CO\cdot CHBr\cdot CH_2Br$, trichloronitromethane (chloropicrin), $CCl_3\cdot NO_2$, diphenylchloroarsine, $AsPh_2Cl$, dichloromethyl ether, $(CH_2Cl)_2O$, *phenylcarbylamine chloride*, $PhN:CCl_2$; (2) in grenades, bromoacetone, bromine, chloroacetone, chlorosulphonic acid, dimethyl sulphate, methyl chlorosulphonate, sulphur trioxide.

The most satisfactory absorbents used in respirators against these attacks have been: (1) a saturated solution of sodium phenoxide; (2) hexamethylenetetramine (urotropine) used in conjunction with sodium phenoxide and sodium hydroxide; (3) active absorbent charcoal; (4) the latter and alkaline permanganate. W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Phenol in the Human Intestine. M. Rhein (*Biochem. Zeitsch.*, 1917, **84**, 246—263).—The author has succeeded in isolating an organism, which he designates as *Bacterium coli phenologenes*, from the human fæces which is capable of producing phenol from tyrosine. It differs in these respects from the ordinary *coli* bacillus, to which it is similar in all other respects. In the presence of sugars, which are fermented by it, it does not produce phenol. It can also produce phenol from *p*-hydroxybenzoic acid, which is thus indicated as an intermediary product in the formation of phenol from tyrosine. S. B. S.

A Correlation between Bacterial Activity and Lime Requirements of Soils. Firman E. Bear (*Soil Sci.*, 1917, **4**, 433—462).—Pot experiments were conducted with soils having lime requirements varying from 0—0·23% of calcium carbonate,

the latter being applied in amounts ranging from 0·01—2·0% of the weight of the soil. The results indicate that the various groups of soil organisms varied in their response to applications of calcium carbonate. Ammonification proceeded fairly satisfactorily in most of the soils as obtained, but the rate was increased, in most cases, by the addition of moderate amounts of calcium carbonate. The rate of nitrification was almost directly correlated with the amount of calcium carbonate applied, and excessive applications were not injurious to the nitrifying organisms. Nitrogen fixation by non-symbiotic soil organisms was considerably increased by the addition of calcium carbonate, but an application of monocalcium phosphate was also necessary for maximum nitrogen fixation. Nitrogen fixation accompanying the growth of soja beans took place readily in acid soils. It was increased by small applications, but decreased by large applications of calcium carbonate. A good growth of soja beans was obtained in a soil having a lime requirement of 0·15%, but well supplied with acid phosphate or manure. [See, further, *Ind.*, 188A.] W. G.

The Assimilation of Carbon Dioxide. II. Baeyer's Assimilation Hypothesis. The Connecting Link in Carbohydrate Formation. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1917, **50**, 1777—1791. Compare A., 1916, i, 105).—The well-known hypothesis that formaldehyde is the connecting link between carbon dioxide and carbohydrates in the plant, first suggested by Baeyer in 1870, has often been attacked in recent years. Many experiments have been made with the object of detecting formaldehyde in the plant, but even if it were found to be present it would not prove that it had been derived from carbon dioxide, since Spoehr has shown that it may be produced by the photolysis of many vegetable acids (A., 1914, i, 120). From time to time, therefore, theories have been advanced in which other deoxidation products of carbon dioxide, such as oxalic acid and glycollic acid, have been suggested as the initial product.

On examination, it will be found that of all the possible primary products, formaldehyde is the only one in the formation of which the volume of carbon dioxide absorbed would be equal to the volume of oxygen liberated. In other words, the "assimilatory quotient," CO_2/O_2, is 1 in the case of formaldehyde, 1·33 for glycollic acid, 2 for formic acid, and 4 for oxalic acid. If it could be arranged, therefore, to determine this quotient in a trustworthy manner, eliminating respiratory effects and so forth, an answer could be given to the much-debated question.

By a method similar to that described in connexion with the assimilatory activity of leaves with different chlorophyll content (*loc. cit.*), the quotient can be determined with a high degree of accuracy, the experimental error only influencing the second place of decimals, and it is found that the quotient is unity, whether the temperature is 10° or 35°, whether the atmosphere is rich in carbon dioxide or even deprived of oxygen altogether (experiment with

cyclamen), or whether ordinary foliage or succulent leaves like cactus are examined. J. C. W.

An Examination of the Leaves of Adonis Vernalis. FREDERICK W. HEYL, MERRILL C. HART, and JAMES M. SCHMIDT (*J. Amer. Chem. Soc.*, 1918, **40**, 436—453).—Tincture of *Adonis vernalis*, or false hellebore, has been used in recent years in cases of cardiac dropsy and epilepsy. The activity is usually assigned to a digitalis-like glucoside, adonidin, which was first described by Cervello (A., 1882, 1126), but the drug which may be purchased under this name is prepared from the roots (Merck's Index, 1907).

The authors have now made a systematic examination of the leaves, having obtained a considerable quantity from Leipzig. They find that an extract in 95% alcohol is somewhat more toxic than digitalis tincture, the average minimum dose which induces permanent systole of the frog's ventricle at the end of one hour (M.S.D.) being about 0·0045 c.c. per gram body weight. They have failed to obtain any more than the slightest evidence of the presence of adonidin or any glucoside in the leaf, but find that more than 60% of the toxicity is connected with the basic fraction precipitated by phosphotungstic acid.

An extract was made by the percolation of 34 kilos. of dried leaves with cold wood spirit, concentrated to a few litres in a vacuum, and mixed with twice the volume of water. The *aqueous solution* yielded: (1) an ethereal extract containing 0·45 gram of a neutral *substance*, $C_{14}H_{18}O_4$, m. p. 133°; (2) a chloroform extract containing 55 grams of indefinite material; (3) a lead acetate precipitate, from which nearly 18 grams of a lemon-yellow *acid*, $C_{31}H_{32}O_{16}$, crystallising from pyridine in plates with 1·5 mols. of solvent, and forming a *deca-acetate*, m. p. 191—192°, was recovered; *d*-glucosazone, corresponding with 1·2% of lævulose in the drug; a phosphotungstic acid precipitate, from which choline equivalent to 0·025% of the drug was recovered (this also contained the principal toxic substance, although efforts to isolate it were not successful), and 2·4% of adonitol, which is the pentitol corresponding with ribose. The *resin* yielded phytosterolin, pentriacontane, myricyl alcohol, phytosterol mixed with a lower homologue, and linolic and palmitic acids. J. C. W.

Transformations of Inulin in the Tuber of the Jerusalem Artichoke during its Period of Rest. H. COLIN (*Compt. rend.*, 1918, **166**, 305—307).—During the winter months, the inulin is gradually converted into sucrose and levulosans, which have a lower specific rotation than inulin and are hydrolysed by invertase, and consequently are fermented by yeast. W. G.

Organic Chemistry.

Preparation of Paraffins. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296741; from *Chem. Zentr.*, 1917, i, 611).—Alcohols are converted into their formates, and these are heated. Thus, *dihydrocholesteryl formate*, narrow tablets, m. p. 84°, when heated at 290°/10 mm., yields cholestane, and myricyl alcohol gives triacontane. The products are purified by mixing the ethereal solutions with acetic anhydride and concentrated sulphuric acid, and evaporating the ether, when the pure hydrocarbons separate.

J. C. W.

Some Reactions of Acetylene. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1918, **37**, 86—87T).—Iron, nickel, cobalt, and to a less extent manganese, tungsten, platinum, and palladium, react with acetylene when heated in this gas or in a mixture of the same with an inert gas. More or less carburisation of the metal results, and at the same time some of the metal enters into the soot-like deposit around the metal. This volatilisation of the metal is practically complete in the case of nickel when the heating is prolonged for a few hours; the soot contains up to 15% of nickel, whilst in experiments with iron it contains 3% of the metal. The carburisation of iron by acetylene is very rapid above 800°, and iron, nickel, and cobalt are still more rapidly carburised by a mixture of ammonia and acetylene. Iron is converted into its nitride by heating it at 800° in ammonia; the nitride when heated in acetylene loses its nitrogen, and the iron becomes highly carburised. Cadmium, zinc, lead, tin, copper, and aluminium do not react with acetylene when heated in this gas. Benzene, toluene, phenol, aniline, naphthalene, etc., behave in a similar manner to acetylene when their vapours are passed over heated nickel or iron.

W. P. S.

The Chemical Actions of the Penetrating Radium Radiation. X. The Influence of the Penetrating Rays on Chloroform and Carbon Tetrachloride. The Action of Ultraviolet Light on Chloroform. ANTON KAILAN (*Monatsh.*, 1917, **38**, 537—552. Compare Hardy and Willcock, A., 1903, ii, 622; Jorissen and Ringer, A., 1907, ii, 520).—The effect of the silent electric discharge alone (Losanitsch, A., 1910, i, 1) and in the presence of hydrogen (Besson and Fournier, A., 1910, i, 349) on chloroform has already been examined. It is now shown that the chief product of the action of the penetrating radium rays for three years on chloroform is hexachloroethane, formed probably by oxidation of the chloroform; chlorine is also produced, but almost completely disappears again by converting the chloroform into carbon tetrachloride and hydrogen chloride. During the exposure, the

chloroform became slightly turbid, and showed an alteration from $D_4^{25 \cdot 1}$ 1·4731 to 1·4755. With carbon tetrachloride, the density increased from D_4^{25} 1·5843 to 1·5845, and the main chemical alteration was the formation of chlorine and hydrogen chloride, the latter being produced by the action of moisture on transiently existent carbonyl chloride, which together with chlorine is produced by the action of oxygen on the carbon tetrachloride; a small quantity of hexachloroethane was also obtained, doubtless by the reaction $2CCl_4 = C_2Cl_6 + Cl_2$. A mixture of β- and γ-rays, and also γ-rays alone, produce a slight effect on chloroform, an increase in density being perceptible. The three years' exposure to the penetrating rays indicated a comparable degree of susceptibility of chloroform and carbon tetrachloride, but the total amount of decomposition in each case was less than 1%. Ultra-violet radiation exerted a similar but more rapid effect than radium radiation on chloroform; the chloroform became turbid and changed from D_4^{25} 1·4744 to 1·4762 in one day; hydrogen chloride, hexachloroethane, and an amorphous, reddish-brown solid were detected in the liquid.

D. F. T.

Liberation of Hydrogen Chloride from Trichloroethylene. W. ELSNER (*Chem. Zeit.*, 1917, **41**, 901—902).—In the recovery of trichloroethylene, which had been used to dissolve resin, it was found that a considerable quantity of hydrogen chloride was formed by the decomposition of the solvent. This decomposition was not brought about by the presence of metals, since the distillation was carried out in glass apparatus, and it was evidently due to the action of resin acids and a small quantity of water. The quantity of hydrogen chloride formed amounted to about 5% of the weight of the solvent.

W. P. S.

History of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1917, **41**, 865, 883—885, 909—911).—A description of the earlier writings on the preparation of alcohol with some sixty-seven references to literature.

W. P. S.

Alcohol and Soda Lime. BURT H. CARROLL (*J. Physical Chem.*, 1918, **22**, 128—149).—When the vapour of ethyl alcohol is passed over soda lime heated at temperatures between 250° and 450°, reaction takes place in accordance with the equation $C_2H_5{\cdot}OH + NaOH = CH_3{\cdot}CO_2Na + 2H_2$. The secondary reaction, $CH_3{\cdot}CO_2Na + NaOH = Na_2CO_3 + CH_4$, begins at about the same temperature, and increases so rapidly with the temperature that at 450° the acetate is decomposed almost as quickly as it is formed. It is found that the sodium hydroxide is the active constituent of the soda lime. At the temperatures used, lime was found to have but little effect on the alcohol, whereas sodium hydroxide reacts more quickly than soda lime. The advantage of using soda lime in preference to sodium hydroxide for the experiments is to be found in the fact that the hydroxide is liquid at the temperatures employed.

It is probable that the conversion of alcohol into acetate involves

three stages, in the first of which acetaldehyde is formed, the sodium hydroxide acting as catalyst. Acetaldehyde is, in fact, found amongst the products when sodium hydroxide is used. Special experiments made with acetaldehyde have shown that this is rapidly decomposed in presence of sodium hydroxide, and it is supposed that the acetaldehyde formed in the first stage is then decomposed according to the equation $CH_3{\cdot}COH = CH_2{:}CO + H_2$, with the formation of keten. The keten then reacts with the sodium hydroxide to form sodium acetate, $CH_2{:}CO + NaOH = CH_3{\cdot}CO_2Na$. The formation of keten has not actually been shown, but this is considered to be the probable course of the reaction. H. M. D.

Preparation of Acetic Acid from Acetaldehyde. Badische Anilin- & Soda-Fabrik (D.R.-P., 296282, addition to 294724; from *Chem. Zentr.*, 1917, i, 461. Compare A., 1917, i, 377).—Instead of iron compounds, such substances as nickel acetate or animal charcoal may be used as catalysts. J. C. W.

The Scale of Influence of Substituents in Paraffin Monobasic Acids and the Correlation of Ionisation with Structure. III. The Bivalent Oxygen Atom in the ε-Position. C. G. Derick and R. W. Hess (*J. Amer. Chem. Soc.*, 1918, **40**, 537—558).—After replying to the criticism by Wegscheider (A., 1912, ii, 529) of the "place factor" and "rule of thirds" mentioned in earlier papers (Derick, A., 1911, ii, 712; 1912, i, 188), and giving recalculated ionisation constants for various organic acids based on modern conductance units, an investigation of the ionisation constant of ε-keto-*n*-heptoic acid is described. From the determined value $1{\cdot}926 \times 10^{-5}$ for the ionisation constant of this acid and a value $1{\cdot}4 \times 10^{-5}$ chosen from earlier results as approximating to the ionisation constant of *n*-heptoic acid (Franke, A., 1895, ii, 252; Drucker, A., 1905, ii, 680), the "relative place influence" of the ε-ketonic oxygen atom, indicating its influence relative to that of the two corresponding hydrogen atoms in *n*-heptoic acid, is calculated to be 0·14.

The requisite ε-keto-n-heptoic acid was prepared by starting from trimethylene glycol, converting this by the action of excess of hydrobromic acid into trimethylene bromide, which on reaction in methyl alcohol with a semi-molecular proportion of potassium cyanide yielded γ-bromobutyronitrile. This product was caused to undergo condensation with ethyl sodioacetoacetate, with formation of *ethyl δ-cyano-α-acetovalerate*, $CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et$, a colourless, viscous liquid, b. p. 154°/2 mm., accompanied by some *ethyl αη-dicyano-δ-acetyl-*n*-heptane-δ-carboxylate*,

$$CO_2Et{\cdot}CAc(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN)_2,$$

a colourless solid of nutty odour, m. p. 76·5°, b. p. approx. 200°/5 mm. The former on hydrolysis with hydrochloric acid gave ethyl alcohol, carbon dioxide, ammonia, and ε-keto-*n*-heptoic acid, $CH_2Ac{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, b. p. 181—182°/25 mm., 160°/13 mm., m. p. 36·5° (compare Perkin, T., 1890, **57**, 230; Blaise and Köhler, A., 1909, i, 204). D. F. T.

Production of Organic Compounds containing Phosphorus. J. D. RIEDEL (D.R.-P., 299992; from *Chem. Zentr.*, 1917, ii, 510).—Unsaturated hydroxy-fatty acids of high molecular weight on treatment with phosphorus trihaloids or oxyhaloids yield as primary products acid haloids in which the hydroxyl group is intact; on hydrolysis of these products with water, phosphorus derivatives of the hydroxy-acids are obtained which may be converted into the salts of the alkaline earth metals in the usual way. Ricinstearolic acid and ricinolic acid on treatment with phosphorus trichloride or tribromide yield *compounds* $C_{18}H_{33}O_5P$ and $C_{18}H_{35}O_5P$ respectively. D. F. T.

The Formation and Decomposition of some Organic Halogenated Compounds. II. EINAR BIILMANN (*Rec. trav. chim.*, 1918, **37**, 245—250. Compare A., 1917, i, 378).—The action of potassium iodide on dibromosuccinic acid in the presence of sulphuric acid is shown to be bimolecular, the product being fumaric acid. The reaction with *iso*dibromosuccinic acid could not be followed quantitatively, owing to the rapidity with which this acid decomposes, giving hydrogen bromide. With benzylbromomalonic acid the action is $CH_2Ph\cdot CBr(CO_2H)_2 + 3KI + H_2O = CH_2Ph\cdot CH(CO_2H)_2 + KI_3 + KBr + KOH$, but a velocity constant for the reaction could not be determined, since the iodine acted on the benzylmalonic acid formed. W. G.

The Nature of the Inositol Phosphoric Acids of some Important Feeding Materials. J. B. RATHER (*J. Amer. Chem. Soc.*, 1918, **40**, 523—536. Compare A., 1917, i, 315).—By hydrolysis of wheat bran with dilute hydrochloric acid, it is possible to obtain an acid, $C_{12}H_{41}O_{42}P_9$ or $C_6H_6(OH)(H_2PO_4)_5$, m. p. 215—216°, which can be separated from accompanying products by means of its strychnine salt, m. p. 220—222°; the latter of the two possible formulæ is preferred, and the compound is described as inositol pentaphosphoric acid; the *silver* salt is amorphous. The method described by Anderson as yielding an inositol hexaphosphoric acid (*N.Y. Geneva Expt. Sta. Tech. Bull.*, 40) is shown to give the pentaphosphoric acid as the main product. Experiments with maize, rice bran, oats, kafir corn, wheat shorts, and rice polish show the principal inositol phosphoric acid to correspond with the above composition. It is possible that other inositol phosphoric acids may be formed from these materials, but the inositol pentaphosphoric acid, together with orthophosphoric acid, constitute on the average 95% of the acid-soluble phosphorus. D. F. T.

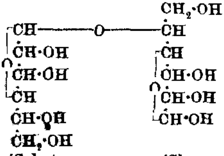
The Non-formation of an *o*-Tolylhydrazone of Lactose, an Affirmation of its Molecular Structure, and on its Indirect Identification. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1918, **37**, 251—253).—The disaccharides, sucrose, maltose, and lactose, and the trisaccharides, trehalose and raffinose, do not yield *o*-tolylhydrazones. This result is considered to support Fischer's view as to the constitution of lactose (compare *Ber.*, 1893, **26**,

2400). Sugars, which on hydrolysis yield galactose, may be detected by hydrolysing them and preparing galactose-*o*-tolylhydrazone (compare A., 1917, ii, 515) from the hydrolysate.

W. G.

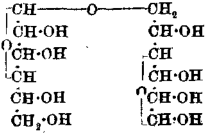
Constitution of the Disaccharides. II. Lactose and Melibiose. WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1918, **113**, 188—199).—A study of the methylation of lactose, and of the hydrolysis of the product, has provided evidence which, with the previously known reactions of the disaccharide, is sufficient to establish the exact constitution of lactose and to make practically certain the structure of melibiose. Methylation is effected by means of methyl sulphate and sodium hydroxide at 30—40°, and the *heptamethyl methyllactoside* so formed yields tetramethylgalactose and a trimethylglucose on hydrolysis with 5% hydrochloric acid at 98°, these being separated by taking advantage of the fact that the former gives an insoluble anilide (Irvine, T., 1910, **97**, 1454). The *trimethylglucose* is stable towards permanganate, and so must be a γ-oxide; it reduces Fehling's solution, it does not form an osazone, and is not identical with Purdie and Bridgett's compound (T., 1903, **83**, 1039), which has the group $-CH_2\cdot OH$ at the end of the chain, thus limiting it to one of two isomerides.

Now, since lactose forms an osazone, and lactobionic acid yields galactose and gluconic acid on hydrolysis, it follows that the reducing group of the glucose residue is free and the adjacent hydroxyl also. The next hydroxyl must also be free, since the galacto-arabinose obtained by the degradation of lactose (Ruff and Ollendorff, A., 1900, i, 476) also forms an osazone. At the fourth carbon atom of the glucose fragment there can be no hydroxyl group, for the above trimethylglucose is γ-oxidic, and as this ether does not contain a free hydroxyl group in the sixth position, it follows that the attachment of the galactose residue to the glucose system in lactose is at the fifth carbon atom. Thus, formula I represents lactose, and, consequently, melibiose is most probably represented by formula II.



(Galactose residue.) (Glucose residue.)

(I.)



(II.)

This conclusion possesses the novel feature that a disaccharide is represented as having a branched chain. It is probable that the

existence of four reducing disaccharides containing two glucose residues is to be explained on similar grounds.

[For experimental details and other arguments, see the original.]

J. C. W.

A Reinvestigation of the Cellulose-Dextrose Relationship. MARY CUNNINGHAM (T., 1918, **113**, 173—181).—The commonly accepted opinion that cellulose is a polydextrose anhydride is based on the assumption that cellulose is quantitatively resolved into dextrose on hydrolysis. The evidence in favour of this view is not based on the isolation of dextrose in quantitative yield, but on the rotation and reducing power of the solutions (compare Willstätter and Zechmeister, A., 1913, i, 955).

It is now shown that such evidence is inadmissible, for cotton and esparto celluloses, although widely different types, give identical optical data on hydrolysis by 40% hydrochloric acid, and an acid of this concentration is known to produce constitutional changes in the simple hexoses themselves. Actual isolation and identification of the products of the hydrolysis, or simple derivatives of them, should be aimed at in such problems.

The author has therefore studied the hydrolysis of cotton and esparto cellulose by sulphuric acid dihydrate and 40% hydrochloric acid, and finds that the products are really esters of polysaccharides which contain acidic hydroxyl groups, and consequently may be isolated as barium or lead salts. No dextrose could be detected, even if the salts were heated with dilute acids, this having the effect of producing further condensation and not hydrolysis. Esparto cellulose is largely furfuroid, but the yield of furfuraldehyde obtained on distilling the diluted solution of the material is lower the longer the diluted liquid is kept, this pointing again to further condensation and not to hydrolysis. J. C. W.

Esparto Cellulose and the Problems of Constitution. CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN (T., 1918, **113**, 182—187. Compare preceding abstract).—Esparto cellulose differs from other celluloses in giving rose-red colorations with aromatic amines and in yielding a constant high proportion (12·5%) of furfuraldehyde when decomposed by acids. It is isolated from the raw material by digesting with 17% of its weight of 3—4% sodium hydroxide at 130°, which treatment has no influence on the furfuroid content. The liquor contains, however, a colloidal furfuroid which yields as much as 50% of furfuraldehyde on boiling with hydrochloric acid. When the purified cellulose is treated with "mercerising soda" (17·5% sodium hydroxide) at 15—20°, or acetylated, or left with sulphuric acid di- or tri-hydrate, or when the concentrated, colloidal furfuroid is digested with sulphuric acid dihydrate, the furfuroid groups suffer change, for the yield of furfuraldehyde from the various products is reduced to about 7·5—8·5%. This renders doubtful the usual assumption that the furfuroids of esparto are pentosans, and coupled with the fact that

cellulose yields stable sulphates and chlorides, which hexoses and their anhydrides do not, it follows that the conception of cellulose as a complex of actual hexosan, or hexosan–pentosan, groups is no longer tenable. J. C. W.

Constitution of the Pectin Substances. TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **85**, 118—161. Compare A., 1915, i, 705, 774).—The pectin substances were obtained from various fruits by treating the same first with hot alcohol and then with water at 125°. To the aqueous extract were then added alcohol and hydrochloric acid, and the pectin was precipitated as a gelatinous mass. On treatment with sodium hydroxide, scission of methyl alcohol to the extent of 7—11% takes place, and the pectin is converted into pectic acid. Pectin is soluble in water, and various preparations yielded furfuraldehyde corresponding with between 35% and 46% of arabinose and 6% and 10% of methyl pentose.

Pectic acid is sparingly soluble in hot water, giving colloidal solutions which are flocculated by salts.

Experiments on fruit jellies indicate that these owe their existence to the combined presence of sugar, pectin, and salts. The so-called bassorin of gum tragacanth also yields methyl alcohol on treatment with sodium hydroxide, and is converted into bassoric acid, which differs from pectic acid in that it is readily soluble in water. S. B. S.

Mechanism of the Electrochemical Synthesis of Carbamide. FR. FICHTER (*Zeitsch. Elektrochem.*, 1918, **24**, 41—45).—The author has carried out a number of experiments with the object of explaining the mechanism of the formation of carbamide at the anode in the electrolysis of a solution of ammonium carbonate (Drechsel, A., 1881, 192). It is shown that this synthesis can also be effected by the action of oxidising agents (ozonised oxygen, hydrogen peroxide, or calcium permanganate) on a concentrated solution of ammonium carbonate in concentrated ammonia. The hypothesis previously put forward to explain the reaction is therefore inadequate. The main change in all the reactions is the oxidation of ammonia to ammonium nitrite and nitrate. During the oxidation, at the anode or at the surface of contact with the oxidising agent, heat is set free, which is removed by external cooling to prevent loss of ammonia. This local elevation of temperature converts a portion of the ammonium carbonate into carbamide. The anodic and chemical formation of carbamide are therefore fundamentally the same as the formation in the living organism. The formation of carbamide from ammonium carbonate or ammonium carbamate is expressed by the equations

$$NH_2{\cdot}CO_2{\cdot}NH_4 + H_2O \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons CO(NH_2)_2 + 2H_2O.$$

At and above 135°, ammonium carbamate cannot exist in the presence of water, consequently at this temperature and above only the right half of the equation comes into operation; with falling temperature, the equilibrium shifts to the right. Below 135°, an

increasing proportion of the ammonium carbonate is converted into the more stable carbamate, and is therefore withdrawn from the reaction if the carbonate is not stabilised by the addition of water. The lower the temperature the greater is the amount of water necessary to make the formation of carbamide possible. The best solution for carbamide formation consists of 1 mol. of ammonium carbamate and 9 mols. of water, and on the assumption that the local temperature elevation does not exceed 100°, calculations of the yield of carbamide do not contradict the hypothesis, inasmuch as the actual yields are much below the calculated values. The results show that ammonium carbonate only can be directly converted into carbamide. J. F. S.

The Direct Conversion of Nitriles into Esters. L. SPIEGEL [with H. SZYDLOWSKY] (*Ber.*, 1918, **51**, 296—298).—The authors have found that the best conditions for the preparation of ethyl esters from nitriles are, generally speaking, treatment with one molecular proportion of concentrated sulphuric acid and ten of alcohol, at 130—140°, in a sealed tube. The lower aliphatic nitriles give equally good results, and in the aromatic series the only hindrance which is recorded is a methyl group in the ortho-position. J. C. W.

The Three Trichlorobenzenes and their Reaction with Sodium Methoxide. A. F. HOLLEMAN (*Rec. trav. chim.*, 1918, **37**, 195—204).—1:2:3-Trichlorobenzene, m. p. 52°, was prepared from 2:6-dichloro-4-nitroaniline by the following series of actions, $NO_2 \cdot C_6H_2Cl_2 \cdot NH_2 \longrightarrow C_6H_2Cl_3 \cdot NO_2 \longrightarrow C_6H_2Cl_3 \cdot NH_2 \longrightarrow C_6H_3Cl_3$, the intermediate products not being isolated. 1:3:5-Trichlorobenzene, m. p. 63°, was prepared from the same starting material by the series of actions $NO_2 \cdot C_6H_2Cl_2 \cdot NH_2 \longrightarrow C_6H_3Cl_2 \cdot NO_2 \longrightarrow C_6H_3Cl_2 \cdot NH_2 \longrightarrow C_6H_3Cl_3$. The three trichlorobenzenes were heated separately in sealed tubes at 180° with a solution of sodium methoxide, the 1:2:3-isomeride yielding 2:3-dichlorophenol, 2:6-dichlorophenol, and a certain amount of the corresponding anisoles; the 1:2:4-isomeride yielded 2:5-dichlorophenol with a small amount of 2:5-dichloroanisole, and the 1:3:5-isomeride yielded 3:5-dichloroanisole as the principal product with a small amount of 3:5-dichlorophenol. The velocity of reaction of the three trichlorobenzenes with sodium methoxide is much greater than that of the three dichlorobenzenes with the same reagent, the 1:3:5-isomeride being the most easily attacked. W. G.

A Reaction of Aromatic Nitro-compounds. S. C. J. OLIVIER (*Rec. trav. chim.*, 1918, **37**, 241—244).—The author has examined the behaviour of twelve aromatic compounds having one or more nitro-groups in the benzene nucleus, and finds that in benzene solution they all give with aluminium bromide an orange-red coloration which disappears on the addition of water. It is suggested that the coloration is due to the loose combination of the aluminium bromide with the nitro-group. In the absence of a solvent or

on replacing the benzene by carbon disulphide, the characteristic coloration is not given in most cases. W. G.

Preparation of Derivatives of the 9:10-Dichloroanthracenes. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 296019; from *Chem. Zentr.*, 1917, i, 460).—The 9:10-dichloroanthracenes combine directly with nitric acid in indifferent, cold media, giving well-defined, crystalline products, probably of the formula $C_6H_4<\begin{matrix}CCl(OH)\\CCl(NO_2)\end{matrix}>C_6H_4$. These decompose most readily, especially on warming with concentrated sulphuric acid, or organic solvents or diluents, giving anthraquinones.

Thus, 9:10-dichloroanthracene itself gives the above *additive* compound, which crystallises in very pale yellow needles, and decomposes at 90—95° into anthraquinone. 2:9:10-Trichloroanthracene yields a similar nitric acid compound, which gives 2-chloroanthraquinone, m. p. 204—206°, on decomposition. J. C. W.

Limits of Accuracy of Holleman's Method of Determining the Composition of a Mixture of Two or Three Isomerides. JOSEPH B. NICHOLS (*J. Amer. Chem. Soc.*, 1918, **40**, 400—403).—A method, proposed by Holleman (Die direkte Einführung von Substituenten in den Benzolkern, 1910), for the estimation of the components in a mixture of three isomerides has been submitted to examination by experiments with certain mixtures of *o*-, *m*-, and *p*-nitroanilines.

The results obtained show that the addition of *o*-nitroaniline in small quantities lowers the eutectic temperature (86·7°) which is characteristic of the binary system *m*-nitroaniline + *p*-nitroaniline to an extent which is nearly proportional to the amount of *o*-nitroaniline added. It is further found that the freezing point of p-nitroaniline is depressed by *m*-nitroaniline to an extent which is not appreciably altered when a small proportion of the *m*-nitroaniline is replaced by *o*-nitroaniline. By combining observations of the freezing point and the eutectic point, it is thus possible to estimate the proportion of *o*-, *m*-, and *p*-nitroanilines in certain mixtures of these isomerides.

The *p*-nitroaniline branch of the freezing curve for mixtures of *m*- and *p*-nitroaniline has been determined. The temperature falls from 146·99° to 97·21° when the addition of the meta-compound amounts to 48·9%. [Compare also *Ind.*, May.] H. M. D.

New Method of Preparation of Monomethylaniline and Dimethylaniline by Catalysis. ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 467—469).—Aluminium oxide is the most satisfactory catalyst for the dehydration. If the vapours of aniline and methyl alcohol in slight excess are passed over this oxide at 400—430°, a mixture of methyl- and dimethylanilines is obtained, and the methylation may be completed by further passage of the methylaniline and methyl alcohol over the catalyst. [See also *Ind.*, May.] W. G.

New Preparation of the Methyltoluidines by Catalysis. ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 564—566).—The method used for the preparation of methyl- and dimethyl-anilines (compare preceding abstract) is equally satisfactory for the preparation of the methyltoluidines. If the vapours of either *o*-, *m*-, or *p*-toluidine and methyl alcohol are passed over aluminium oxide at 350—400°, a mixture of methyl- and dimethyl-toluidines is obtained. A second treatment converts this mixture entirely into the tertiary base. [See also *Ind.*, May.] W. G.

Separation of Secondary Arylamines from Primary Amines. TUDOR WILLIAMS PRICE (*J. Soc. Chem. Ind.*, 1918, **37**, 82—84T).—The method depends essentially on the fact that the sulphates of primary amines are insoluble in the free bases, whilst those of *sec.*- and *tert.*-amines are soluble in an excess of the free amines (compare Gnehm and Blumer, *ibid.*, 1899, **18**, 129). It is particularly adaptable to the recovery of unchanged base from the mixture obtained by heating an aromatic amine with an alcohol in the presence of a condensing agent, for the quantity of primary amine to be removed is usually not excessive.

The mixture is treated with sufficient concentrated sulphuric acid to combine with the primary amine (determined by titration), when this is almost completely precipitated as sulphate. A repetition of the process may be advisable. Considerable quantities of the alkylated base are carried down with the precipitate, so this is economically washed with the alcohol employed in the reaction. The recovered alcohol and sulphate may then be used in a second charge. J. C. W.

Production of Aromatic Selenium Compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 299510; from *Chem. Zentr.*, 1917, ii, 509—510).—Organic selenium compounds can be prepared by treating such substances as aniline, acetanilide, phenol, salicylic acid, and nitrophenol with a solution of selenium or selenium dioxide in sulphuric acid at low temperature. The product from acetanilide forms colourless crystals, m. p. approx. 260°; colourless products were also obtained from phenol, salicylic acid, and resorcinolarsinic acid, whereas aniline sulphate yielded an almost black powder and *o*- and *p*-nitrophenols yellow products. The *compound*, needles, m. p. 260° (decomp.), produced from *p*-acetylaminophenetidine had the composition

$$(OEt{\cdot}C_6H_3{\cdot}NHAc)_2SeSO_4H,H_2O,$$

whilst antipyrine yielded a *diantipyryl selenide*, $(C_{11}H_{11}ON_2)_2Se$, colourless needles, m. p. 240° (decomp.). D. F. T.

The Ternary System: Phenol–Acetamide–Ethyl Alcohol and the Binary System: Phenol–Benzamide. Theory of Recrystallisation. ROBERT KREMANN and MAX WENZING (*Monatsh.*, 1918, **39**, 479—500).—When heated with phenol, acetamide and benzamide are converted into phenyl acetate and benzoate respectively, with liberation of ammonia. Doubtless intermediate

additive compounds are formed, because the fusion curve for mixtures of phenol and acetamide shows a maximum m. p. 40·8° at the composition $CH_3 \cdot CO \cdot NH_2, 2C_6H_5 \cdot OH$, this result being interpreted as an indication of the presence of a free valency electron at the carbonyl and also at the amino-group of the amide. Benzamide apparently has a weaker affinity than acetamide towards phenol, the fusion curve for benzamide–phenol showing the occurrence of a compound $C_6H_5 \cdot CO \cdot NH_2, 2C_6H_5 \cdot OH$, but the molten compound is dissociated to such an extent that the maximum m. p. is not observable.

The failure to obtain the compound $CH_3 \cdot CO \cdot NH_2, 2C_6H_5 \cdot OH$ by recrystallisation of a mixture of the two constituents from alcohol is attributed to the relatively low m. p. of the compound, which in the presence of a third substance, such as alcohol, may fall well below the ordinary temperature. A theoretical consideration is *given of the conditions of equilibrium in a ternary system* such as phenol–acetamide–alcohol, the assumption being made that there is no further formation of compounds, either binary or tertiary.

D. F. T.

Solubility of Salts of Nitrophenols in Mixtures of Alcohol and Water. W. M. FISCHER (*Zeitsch. physikal. Chem.*, 1918, **92**, 581—599).—The solubility of sodium picrate, $C_6H_2(NO_2)_3 \cdot ONa, H_2O$, in mixtures of water and ethyl alcohol at 0° and 25° varies with the composition of the solvent in a remarkable way, in that the *curve shows a maximum and two minima.* The *maximum occurs* at about 50% of alcohol by volume and the minima at about 25% and 95—99% respectively.

The anomalous form of the curve has led to the investigation of the solubility of other salts of nitrophenols, including potassium picrate, barium picrate, the sodium salts of *p*-nitrophenol, 2:4-dinitrophenol, and 2-chloro-4-nitrophenol, and also barium dinitrosalicylate. The results indicate that the curve is of the same type in all these cases, showing a maximum and two minima. It is suggested that the anomalous solubility curve is due to the *existence of two isomeric forms of the salts, the equilibrium between* which is displaced as the proportion of alcohol to water is changed. As evidence in support of this view, preliminary measurements of the extinction coefficients for solutions of salts of the nitrophenols in mixtures of ethyl alcohol and water are adduced which show that the absorption is not by any means a linear function of the composition of the solvent.

The solubility curves for potassium picrate and the sodium salt of 2:4-dinitrophenol exhibit a maximum in mixtures of acetone and water and a minimum in mixtures of methyl alcohol and water.

H. M. D.

The Salts of the Complex Acid: Catechol-Boric Acid. J. BÖESEKEN [with A. OBBEEN and (MLLE.) A. VAN HAEFTEN] (*Rec. trav. chim.*, 1918, **37**, 184—194).—The two metallic and the ammonium salts were prepared by shaking concentrated solutions

of boric acid, catechol, and the respective hydroxide together in the molecular proportions 1:2:1. The three salts separated in the form of white leaflets. The salts of the organic bases were similarly prepared, the salts crystallising in needles. The following salts were prepared: *ammonium* salt, $(C_6H_4O_2)_3B_2O_4(NH_4)_2$; *potassium* salt, $(C_6H_4O_2)_3B_2O_4K_3$ or $(C_6H_4O_2)_3B_2O_4H_2K_2$; *rubidium* salt, analytical results not satisfactory; *aniline* salt, constitution not settled; *dimethylaniline* salt, $(C_6H_4O_2)_3BO_4H_2(C_6H_4{\cdot}NMe_2),5H_2O$ [?]; p-*chloroaniline* salt, $(C_6H_4O_2)_2B_3O_3(C_6H_4Cl{\cdot}NH_2)_3,4H_2O$ [?].

W. G.

Methylation with Methyl Sulphate, Hydrolysis of Methyl Sulphate with Aqueous Alkali and Water in a Heterogeneous System, and a Case of Potassium Catalysis. ALFONS KLEMENC [with EMMA EDHOFER] (*Monatsh.*, 1918, **38**, 553—580).—The unequal behaviour of potassium and sodium salts has occasionally been observed, for example, in the better yield of methyl benzoate obtained by the reaction of methyl sulphate with potassium benzoate than with sodium benzoate (Graebe, A., 1905, i, 678), and the better methylation of potassium benzoate by potassium methyl sulphate than by sodium methyl sulphate. It is now shown that in the methylation of phenolic hydroxyl, for example, in quinol or resorcinol, the use of potassium hydroxide gives much poorer yields than sodium hydroxide. Physicochemical considerations exclude the possibility that the difference is to be attributed to the different rates of diffusion of the two hydroxides from one phase to another in the heterogeneous system, and indicate that the hydrolysis occurs in a homogeneous system containing the dissolved ester. Any possible difference in the solubility of methyl sulphate in aqueous solutions of the respective alkalis is insufficient to account for the inequality in their effect. The probable explanation is that potassium hydroxide effects a more rapid hydrolysis of methyl sulphate than sodium hydroxide of equivalent concentration, on account of a catalytic influence of the undissociated potassium hydroxide molecules, in confirmation of which it is found that the addition of potassium chloride to a solution of sodium hydroxide raises the hydrolysis constant, whereas the addition of sodium chloride depresses it; on the other hand, the addition of potassium chloride to potassium hydroxide solution also depresses the hydrolysis constant. The conclusion is therefore drawn that during the methylation of a phenol, the undissociated phenoxide and the hydroxyl ions react concurrently and independently with the methyl sulphate, and that the poorer yield of methoxy-derivative obtained with the use of potassium hydroxide is due to the catalytic acceleration of the latter reaction.

D. F. T.

6-Thiol-β-naphthol. TH. ZINCKE and R. DERESER (*Ber.*, 1918, **51**, 352—360).—The preparation of 6-thiol-β-naphthol and its more important derivatives is described (compare the 4- and 5-thiol-α-naphthols, A., 1915, i, 135, 531).

β-Naphthol-6-sulphonic acid is converted by means of ethyl chloroformate into *sodium 2-ethylcarbonatonaphthalene-6-sulphonate*, pearly leaflets, and this into the sulphonyl *chloride*, m. p. 118°, and then into *2-ethylcarbonatonaphthalene-6-sulphonanilide*, $CO_2Et{\cdot}O{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NHPh$, bundles of needles, m. p. 130°, which may be hydrolysed to *β-naphthol-6-sulphonanilide*, m. p. 105°. The sulphonyl chloride is reduced by means of zinc dust and hydrochloric acid to *2-ethylcarbonatonaphthalene-6-thiol*,

$$CO_2Et{\cdot}O{\cdot}C_{10}H_6{\cdot}SH,$$

which crystallises in glistening scales, m. p. 87°, and may be reconverted into the sulphonyl chloride by treatment with chlorine. The thiol forms an *acetate*, m. p. 95°, and may be oxidised by alcoholic ferric chloride to *di-2-ethylcarbonato-6-naphthyl disulphide*, $(CO_2Et{\cdot}O{\cdot}C_{10}H_6)_2S_2$, glistening scales, m. p. 127°. It also reacts with methyl sulphate to form *2-ethylcarbonato-6-naphthyl methyl sulphide*, $CO_2Et{\cdot}O{\cdot}C_{10}H_6{\cdot}SMe$, which crystallises in long, glistening needles, m. p. 97°, reacts with chlorine to form an obscure *tetrachloride*, m. p. 167—172°, and may be oxidised by means of hydrogen peroxide to the corresponding *sulphoxide*,

$$CO_2Et{\cdot}O{\cdot}C_{10}H_6{\cdot}SMeO,$$

scales, m. p. 67°, or *sulphone*, $CO_2Et{\cdot}O{\cdot}C_{10}H_6{\cdot}SMeO_2$, scales, m. p. 98°.

6-*Thiol-β-naphthol* is obtained by hydrolysing the above ethyl carbonatonaphthalenethiol. It crystallises in odourless leaflets, m. p. 137°, and forms a *diacetate*, m. p. 107°. The corresponding disulphide, methylthiol, and its sulphoxide and sulphone, are also prepared by hydrolysing the ethylcarbonato-compounds. *Di-β-naphthol-6 disulphide* forms colourless leaflets, m. p. 220—221°, and yields a *diacetate*, m. p. 167—168°; *β-naphthol-6 methyl sulphide* crystallises in silvery leaflets, m. p. 121°, forms an *acetate*, m. p. 74°, may be methylated to *2-methoxy-6-naphthyl methyl sulphide*, m. p. 105—106°, and reacts with bromine to form 1:5-*dibromo-β-naphthol-6 methyl sulphide*, leaflets, m. p. 194—195° (*acetate*, m. p. 145°), and the corresponding *dibromide*,

$$OH{\cdot}C_{10}H_4Br_2{\cdot}SMeBr_2,$$

reddish-brown crystals; *β-naphtholmethyl-6-sulphoxide*,

$$OH{\cdot}C_{10}H_6{\cdot}SMeO,$$

has m. p. 164—165°, and the *sulphone*, $OH{\cdot}C_{10}H_6{\cdot}SMeO_2$, has m. p. 151—152°, and forms an *acetate*, m. p. 145—146°, and *methyl ether*, m. p. 143—144°.

β-Naphthol-6-sulphinic acid, $OH{\cdot}C_{10}H_6{\cdot}SO_2H$, is prepared by adding a mixture of 2-ethylcarbonatonaphthalene-6-sulphonyl chloride and sodium hydrogen carbonate to a warm solution of sodium sulphite. It crystallises in leaflets, decomp. 120—125°, and forms a methyl ester and methyl ether of this, which are identical with the above *β*-naphthol-6-methylsulphone and its methyl ether.

J. C. W.

Preparation of 1 : 8-Dihydroxyanthranol. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296091; from *Chem. Zentr.*, 1917, i, 351).—1 : 8-*Dihydroxyanthranol*, m. p. 178—180°, a valuable

agent in cases of psoriasis and other skin diseases, is prepared by the reduction of 1 : 8-dihydroxyanthraquinone by means of zinc and an acid. J. C. W.

Preparation of Acyl Derivatives of Aminonaphthols and their Sulphonic Acids. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 295767 and 296446; from *Chem. Zentr.*, 1917, i, 293, 546).—Aminonaphthols and their sulphonic acids are treated with 2-hydroxy-3-naphthoyl chloride or its acetyl derivative, giving naphthoylamino-compounds which have a great affinity for cotton and silk. Thus, 2-amino-5-naphthol-7-sulphonic acid yields 2-2'-*hydroxy-3'-naphthoylamino-5-naphthol-7-sulphonic acid*, as an almost colourless, crystalline mass, which is fixed by cotton in an alkaline solution or by silk in acetic acid solution, and may be coupled with diazonium salts on the fibre. 2-2'-*Hydroxy-3'-naphthoylamino-8-naphthol-6-sulphonic acid*, 1-2'-*hydroxy-3'-naphthoylamino-8-naphthol-3 : 6-disulphonic acid*, 1-2'-*acetoxy-3'-naphthoylamino-7-naphthol*, m. p. 198—200°, and 1-2'-*hydroxy-3'-naphthoylamino-7-naphthol*, m. p. 198—200°, are pale grey, crystalline masses or powders. J. C. W.

d-Benzylidenecampholic Acid. HANS RUPE and ALFRED BLECHSCHMIDT (*Ber.*, 1918, **51**, 170—180).—A revision of the work on the action of hydrobromic acid on *d*-benzylidenecamphor described by Haller and Minguin (A., 1900, i, 452).

Benzylidenecamphor is conveniently prepared by treating camphor with sodium in toluene solution, and then adding benzaldehyde and gently boiling in a current of hydrogen. When heated in a pressure bottle at 100° with a solution of hydrogen bromide in slightly diluted acetic acid, saturated at 0°, it is converted into a crystalline acid mixed with a viscous substance. These are separated by boiling with magnesium oxide and water, the viscous substance being chiefly a non-acidic wax, and not benzylidenecampholic acid, as Haller and Minguin suggested. The acid recovered from the magnesium salt is the phenylhydroxyhomocampholic acid described by the French workers, but as it loses water readily on boiling with formic acid, it is supposed to be represented more correctly by the alternative formula,

$$CO_2H\cdot C_8H_{14}\cdot CH(OH)\cdot CH_2Ph.$$

It crystallises from diluted acetic acid in thickly interwoven, stout needles, m. p. 206°, and forms an *ethyl* ester, long needles, m. p. 104°.

d-*Benzylidenecampholic acid*, $CO_2H\cdot C_8H_{14}\cdot CH:CHPh$, is the product of the action of formic acid on the hydroxy-acid. It is purified by distillation, followed by crystallisation from acetic acid (4 acid to 1 water), and is then obtained in asbestos-like masses, m. p. 124—125°, b. p. 228°/11 mm., which yield benzoic and camphoric acids on oxidation with permanganate. The *methyl* ester forms large, star-like groups of needles, m. p. 97·5—98°, and the *ethyl* ester small, glistening prisms, m. p. 95—97°; these are prepared from the chloride, which is obtained by the action of

thionyl chloride. The acid may be hydrogenated in the presence of nickel or colloidal palladium, d-*benzylcampholic acid* being obtained in slender needles, m. p. 119—119·5°, and its *methyl* ester in long, flat needles, m. p. 44°, b. p. 196—197°/13 mm. It also combines with bromine to form *αβ-dibromobenzylcampholic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CHBr{\cdot}CHPhBr$, long needles, m. p. 161°, and with hydrogen bromide in glacial acetic acid to form *α-bromobenzylcampholic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CHBr{\cdot}CH_2Ph$, which crystallises in groups of spiky needles, m. p. 139°, and is also produced in excellent yield when benzylidenecamphor is left for four months with a saturated solution of hydrogen bromide in glacial acetic acid.

J. C. W.

Some Stereoisomerides of Benzylidenementhone Hydrocyanide [Phenylmenthylacetonitrile; Phenylmenthylcyanomethane]. EYVIND BOEDTKER (*Bull. Soc. chim.*, 1918, [iv], **23**, 64—70).—The author has isolated seven stereoisomeric phenylmenthylacetonitriles from the products of the action of potassium cyanide on benzylidenementhone hydrochloride in alcoholic solution (compare A., 1916, i, 51). They have respectively the following properties: (1) slender, yellow needles, m. p. 193°, $[\alpha]_D^{24}$ −83°23′ (in benzene); (2) colourless prisms, m. p. 158°, inactive; (3) colourless prisms, m. p. 148°, $[\alpha]_D^{26}$ +78°7′ (in benzene); (4) colourless plates, m. p. 124°, $[\alpha]_D^{26}$ −53°32′; (5) silky needles, m. p. 183°, $[\alpha]_D^{26}$ −58°51′; (6) slender needles, m. p. 201°, inactive; (7) long needles, m. p. 205°, inactive. If in the preparation of these compounds the reagents are only heated in boiling alcoholic solution for one hour, the main product is the isomeride (1), but if the time of heating is prolonged or a little potassium hydroxide is introduced, the main product is the stable stereoisomeride (6), m. p. 201°.

W. G.

A New Synthesis of Tropic Acid. E. MÜLLER (*Ber.*, 1918, **51**, 252—255).—All syntheses of tropic acid so far attempted have started from compounds, such as acetophenone, in which the $\colon CPh{\cdot}CH_2{\cdot}$ grouping is pre-existent. None of the successful methods can be regarded as simple, but the other alternative, using a compound with the $\cdot CHPh{\cdot}CO_2R$ grouping, is now found to be a most convenient synthesis, which may perhaps be applied to substituted tropic acids.

Ethyl phenylacetate and ethyl formate are condensed in the presence of sodium to form the well-known mixture of desmotropic ethyl formylphenylacetates, and this mixture is reduced by means of aluminium amalgam in moist ether. About half of the formylphenylacetate combines with the sludge of aluminium hydroxide, and can only be recovered after shaking this with dilute sulphuric acid. The ethyl tropate present in the ethereal solution is hydrolysed by warm barium hydroxide solution.

J. C. W.

The Benzoylated Cyanohydrins from Aldehydes and Ketones, and the Corresponding Amides and Acids. J. ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1918, [iv], **23**, 98—101).—By

the methods previously described (compare A., 1912, i, 462; 1913, i, 620, 728; 1916, i, 263), the following benzoylcyanohydrins and the corresponding amides and acids have been obtained.

α-Benzoyloxy-γ-phenyl-Δ^{β}-butenonitrile, $CHPh:CH \cdot CH(OBz) \cdot CN$, m. p. 66—67°, gives the *amide*, $CHPh:CH \cdot CH(OBz) \cdot CO \cdot NH_2$.

α-Benzoyloxy-p-iso*propylphenylacetonitrile*,

$$CHMe_2 \cdot C_6H_4 \cdot CH(OBz) \cdot CN,$$

m. p. 65°, gives the corresponding *amide*, m. p. 182°, which on hydrolysis yields *p-iso*propylphenylglycollic acid.

1-*Benzoyloxy*cyclo*pentane*-1-*carboxylonitrile*, $OBz \cdot C_5H_8 \cdot CN$, m. p. 52—53°, giving the *amide*, $OBz \cdot C_5H_8 \cdot CO \cdot NH_2$, m. p. 111—112°.

The cyanohydrin from heptaldehyde was not isolated. but the oily product, when hydrolysed with dilute sulphuric acid, yielded the *amide*, $CH_3 \cdot [CH_2]_5 \cdot CH(OBz) \cdot CO \cdot NH_2$, m. p. 104—105°.

αβ-Dibenzoyloxysuccinonitrile, $OBz \cdot CH(CN) \cdot CH(OBz) \cdot CN$, m. p. 195—196°, did not yield an amide, but tartaric acid was isolated from the products of hydrolysis. W. G.

New Galloyl Derivatives of Dextrose and Comparison of them with Chebulic Acid. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, **51**, 298—320).—Tri- and mono-galloylglucose have been obtained by means of glucosemonoacetone and glucosediacetone, a method by which partly acylated glucoses have been prepared already (A., 1916, i, 363). These derivatives have been compared very thoroughly with chebulic acid, which is known to yield gallic acid and dextrose on hydrolysis, but the conclusion is drawn that the acid is not related in structure to the galloylglucoses.

Glucosemonoacetone is treated with triacetylgalloyl chloride (this vol., i, 173) and quinoline, diluted with chloroform, and thus converted into *tri-triacetylgalloylglucosemonoacetone*,

$$CMe_2:C_6H_7O_6[CO \cdot C_6H_2(OAc)_3]_3,$$

which is a faintly reddish-yellow powder, $[\alpha]_D^{20}$ −66·5° (in acetone). This is shaken at below 20°, in a current of hydrogen, with dilute sodium hydroxide, alcohol, and ether until solution takes place, when the mixture is exactly neutralised, giving *trigalloylglucosemonoacetone* as an amorphous, leafy mass, $[\alpha]_D^{21}$ −93·32° (in acetone). Dilute solutions of the derivative give deep bluish-violet colours with ferric chloride, and form precipitates with gelatin, brucine, quinine, quinoline, and pyridine. The hydrolytic scission of the *iso*propylidene group is effected by means of 0·5*N*-sulphuric acid at 70°, *trigalloylglucose* being obtained as a tannin-like mass, $[\alpha]_D^{20}$ −118·6° (in acetone), which is bitter and astringent in taste, whereas chebulic acid is sweet, and soluble in ice-cold water, whilst Chinese tannin is very sparingly soluble. A 10% alcoholic solution forms a jelly with 10% acoholic arsenic acid, and towards ferric chloride and bases it behaves like its acetone compound.

The methylcarbonato-derivative of galloyl chloride gives *tri-3:4:5-trimethylcarbonatobenzoylglucoseacetone*,

$$CMe_2:C_6H_7O_6[CO \cdot C_6H_2(O \cdot CO_2Me)_3]_3,$$

in amorphous flocks, $[\alpha]_D^{20}$ −56·25° (in *s*.-tetrachloroethane).

Similarly, the methyl ether yields *tri-3:4:5-trimethoxybenzoylglucoseacetone*, as a colourless powder, $[\alpha]_D^{20}$ −89·30° (in acetone), which does not give a colour with ferric chloride, and may be hydrolysed in the cold by means of concentrated hydrochloric acid dissolved in glacial acetic acid to form *tri-3:4:5-trimethoxybenzoylglucose*, $C_6H_9O_6[CO{\cdot}C_6H_2(OMe)_3]_3$, $[\alpha]_D^{20}$ −92·99° (in acetone). The presence of two free hydroxyl groups in the glucose residue of this may be demonstrated by means of *p*-bromobenzoyl chloride, which, in the presence of quinoline, yields *di-*p*-bromobenzoyltri-3:4:5-trimethoxybenzoylglucose*, a leafy mass, with Br = 14·17%. Trigalloylglucose reacts with diazomethane to give an indefinite methyl derivative, which also reacts with *p*-bromobenzoyl chloride, and as the product contains about 16·8% of bromine, it follows that at least two hydroxyl groups are left unattacked by the reagent. Chebulic acid behaves differently (see below).

Glucosediacetone yields *triacetylgalloylglucosediacetone*,

$$C_6H_7O_6(CMe_2)_2[CO{\cdot}C_6H_2(OAc)_3]_3,$$

in colourless flocks, $[\alpha]_D^{18}$ −30·13° (acetone), from which *galloylglucosediacetone*, $[\alpha]_D^{18}$ −33·82°, *galloylglucosemonoacetone*, $[\alpha]_D^{20}$ −20·22°, and *galloylglucose*, $C_6H_{11}O_6{\cdot}CO{\cdot}C_6H_2(OH)_3$, $[\alpha]_D^{18}$ +46·5° (alcohol), may be obtained as amorphous masses in the usual way. The behaviour of these towards the tannin reagents is described. Galloylglucose gives a deep blue colour with ferric chloride, but does not form precipitates with gelatin or bases. It is not identical with Feist's glucogallic acid (A., 1914, i, 195).

Chebnlic acid, the eutannin of commerce, crystallises well from diluted acetone in needles. That it yields dextrose on hydrolysis with *N*-sulphuric acid has now been proved by the isolation of the osazone and by the fermentation method, but the cleavage proceeds at a much slower rate than is the case with the tri- and pentagalloylglucoses. A methylated chebulic acid may be obtained by the action of diazomethane (compare Richter, A., 1913, i, 989), but the product given by this when treated with *p*-bromobenzoyl chloride only contains abont 9% of bromine. Chebulic acid therefore differs from trigalloylglucose. Furthermore, chebulic acid does not condense with acetone under the influence of hydrogen chloride, whereas tribenzoylglucose does so quite readily.

Tribenzoylglucose reacts in some way with diazomethane, but not to form a methylglucoside, for the product still reduces Fehling's solution. Apparently, also, it does not form an ether, for treatment with *p*-bromobenzoyl chloride, as above, indicates the presence of two free hydroxyl groups. J. C. W.

Partial Acylation of Polyhydric Alcohols and Sugars. IV. Derivatives of *d*-Glucose and *d*-Fructose. EMIL FISCHER and HARTMUT NOTH (*Ber.*, 1918, **51**, 321—352. Compare A., 1916, i, 363—365).—Hitherto, a tribenzoylglucose (*ibid.*, 364) and two stereoisomeric pentabenzoylglucoses (A., 1912, i, 888) have been

described. To these are now added a mono-, di-, and tetra-benzoyl-glucose, prepared by the application of the condensation products of dextrose with acetone. In the case of lævulose, a crystalline, monogalloyl derivative is described, and some acyl derivatives of lævuloseacetone.

Benzoylglucosediacetone, which has now been obtained crystalline, with m. p. 63—64° (corr.), $[\alpha]_D^{18}$ −49·7° (compare A., 1915, i, 118), is left with 2*N*-sulphuric acid and alcohol at 50°, and thus converted into *benzoylglucosemonoacetone*, $CMe_2:C_6H_9O_5\cdot OBz$, a crystalline mass, m. p. 195—197° (corr.), $[\alpha]_D^{20}$ +8·5° (alcohol), which does not reduce Fehling's solution. This is changed into tribenzoylglucosemonoacetone (A., 1916, i, 364) by means of benzoyl chloride and quinoline, and either of the benzoylglucoseacetones may be hydrolysed by means of a mixture of sulphuric and acetic acids at 70° to give *benzoylglucose*, $C_6H_{11}O_5\cdot OBz,H_2O$, which forms stout, glistening crystals, m. p. 104—106° (corr.), $[\alpha]_D^{21}$ +45·76°, +44·57° after twenty-four hours (in water), $[\alpha]_D^{20}$ +47·32°, +49·34° after twenty-four hours (in alcohol). This derivative has as great a reducing power as dextrose, and suffers no weakening of this property when heated at 100° for some hours. It may be condensed with acetone to form benzoylglucosediacetone again, and it reacts with phenylhydrazine in the cold to give a *phenylhydrazone*, pale yellow prisms, m. p. 146—147° (corr.), $[\alpha]_D^{20}$ +11·1° (in pyridine), whilst it yields glucosazone if warmed with this agent.

A substance, which was presumed to be a monobenzoylglucose, is the "vacciniin" isolated by Griebel from the whortleberry (A., 1910, ii, 440). Having been supplied with some residues by Griebel, the present authors have been able to confirm the fact that the above benzoylglucose does actually occur in the natural product. They have not succeeded in isolating the substance, but have obtained a pure specimen of benzoylglucoseacetone from the crude material.

Tetrabenzoylglucose is prepared by the action of silver carbonate on benzobromo-*d*-glucose (A., 1911, i, 803) in moist acetone. An amorphous product is obtained which exhibits mutarotation, and is obviously a mixture of stereoisomerides, but an individual substance, crystallising from much light petroleum in slender needles, m. p. 119—120° (corr.), $[\alpha]_D^{21}$ +70·6° (constant; alcohol), has been isolated. This forms an additive *compound* with pyridine in equimolecular proportions, which has m. p. 103—104° (corr.) and $[\alpha]_D^{24}$ +62·07° (in alcohol).

For the preparation of a dibenzoylglucose, partly acetylated derivatives prove to be the most suitable material. Glucosediacetone is treated with acetic anhydride and pyridine at 0°, and the *acetylglucosediacetone* so formed, in platelets, m. p. 62—63°, $[\alpha]_D^{20}$ −31·5°, which tastes very bitter and does not reduce Fehling's solution, is hydrolysed by a mixture of dilute sulphuric acid and alcohol at 50° to *acetylglucosemonoacetone*, m. p. 144—146° (corr.), $[\alpha]_D^{24}$ −6·27°. This is treated with benzoyl chloride and pyridine, when *acetyldibenzoylglucoseacetone* is obtained, in elongated plate-

lets, m. p. 114—115° (corr.), $[\alpha]_D^{20}$ −73·98° (acetone). When left with a mixture of 5*N*-sulphuric acid and acetone at 90° in a pressure bottle, this loses not only the acetone residue, but the acetyl group as well, and *dibenzoylglucose* is formed. This crystallises from chlorobenzene in short needles or hexagonal platelets, m. p. 145—146° (corr.), $[\alpha]_D^{19}$ in alcohol, +56·2°, +66·7° after six days, and reacts with *p*-bromobenzoyl chloride and pyridine to form *dibenzoyltri*-p-*bromobenzoylglucose*, $[\alpha]_D^{8}$ +32°.

Benzoylfructosediacetone is a crystalline substance, m. p. 107—108° (corr.), $[\alpha]_D^{20}$ −161·2°, which neither reduces Fehling's solution nor reacts with phenylhydrazine, but yields *benzoylfructosemonoacetone* when left with a mixture of acetone and *N*-hydrochloric acid at 50°. This is a very bitter, crystalline material which sinters at about 185°, has m. p. 202—204° (corr.) and $[\alpha]_D^{16}$ −151·64°, and is very sparingly soluble in water. It yields *tribenzoylfructosemonoacetone*, an amorphous solid, which may be hydrolysed to an amorphous *tribenzoylfructose*, $[\alpha]_D^{15}$ −249·75°, this being a powerful reducing sugar.

p-*Bromobenzoylfructosediacetone* crystallises in needles or prisms, m. p. 136—137° (corr.); p-*bromobenzoylfructosemonoacetone* has m. p. 222—225° (corr.); and *tri*-p-*bromobenzoylfructosemonoacetone* is a crystalline compound, with m. p. 142—143° (corr.), $[\alpha]_D^{16}$ in acetone, −365°.

Acetylfructosediacetone crystallises from hot water in long, glistening needles, m. p. 76—77°, $[\alpha]_D^{18}$ −176·3°; *acetylfructosemonoacetone* has m. p. 154—155° (corr.), $[\alpha]_D^{19}$ −180·6°; *triacetylfructosemonoacetone* crystallises in groups of prisms, m. p. 99—101° (corr.), $[\alpha]_D^{23}$ −134·9°; *benzoyldiacetylfructosemonoacetone*, m. p. 77—78°, $[\alpha]_D^{22}$ −132·5°, is very sparingly soluble in water, but freely so in most organic solvents; *dibenzoylacetylfructosemonoacetone* crystallises in platelets, m. p. 108—109° (corr.), $[\alpha]_D^{21}$ −269·4°, and has the same solubilities; and *di*-p-*bromobenzoylacetylfructosemonoacetone*, $CMe_2{:}C_6H_7O_6Ac(CO{\cdot}C_6H_4Br)_2$, forms large crystals, m. p. 146—147° (corr.), $[\alpha]_D^{15}$ −288°.

Fructosediacetone reacts with triacetylgalloyl chloride in the presence of quinoline, giving *triacetylgalloylfructosediacetone*, which crystallises in well-developed prisms or needles, m. p. 157—159° (corr.), $[\alpha]_D^{20}$ −118·17°, and is hydrolysed by shaking with a mixture of alcohol and 2*N*-sodium hydroxide in an atmosphere of hydrogen to *galloylfructosediacetone*, a very bitter, astringent substance, m. p. 199—200° (corr.), $[\alpha]_D^{18}$ −141·24°. The acetone residues may be removed in the usual way, and the product, *galloylfructose*, unlike the benzoyl derivatives, has been obtained crystalline. It forms masses of slender needles, decomp. 150—155°, $[\alpha]_D^{19}$ in water, −80·4°, and behaves like galloylglucose towards tannin reagents, except that it gives a jelly with alcoholic arsenic acid. J. C. W.

Preparation of a 1 : 5-Dihydroxynaphthalenedicarboxylic Acid. FRANZ VON HEMMELMAYR (D.R.-P., 296035; from *Chem. Zentr.*, 1917, i, 351. Compare A., 1917, i, 457).—1 : 5-*Dihydroxy*-

naphthalenedicarboxylic acid is a yellow powder, m. p. about 300° (decomp.), and forms colourless alkali salts, which exhibit blue fluorescence in water and may be easily "salted out." The acid and its salts combine with wool fibres, subsequent treatment with chromic acid or chromates giving very pure brown tones.

J. C. W.

The Mechanism of the Formation of Benzophenone by the Friedel and Crafts' Reaction. S. C. J. OLIVIER (*Rec. trav. chim.*, 1918, **37**, 205—240).—A study of (1) the action of benzoyl chloride on benzene in the presence of aluminium chloride in benzene solution; (2) the action of benzoyl bromide on benzene in the presence of aluminium bromide in benzene solution; (3) the reaction (2), but in carbon disulphide as solvent. Reactiou (1) is unimolecular, and shows a slight but regular fall in the value of K with the time. The presence of an excess of benzoyl chloride is without influence on the reaction. One molecule of aluminium chloride can only transform one molecule of benzoyl chloride, and the action $COPhCl,AlCl_3 + C_6H_6 = COPh_2,AlCl_3 + HCl$ is not reversible. Reaction (2) is also unimolecular, with a slight fall in the value of K, but the velocity of reaction is much greater than with the chlorides. With an excess of aluminium bromide, the velocity of the reaction increases enormously, the excess of this catalyst acting almost proportionately to its concentration. Cryoscopic measurements show that in benzene solution the compound $COPh_2,AlBr_3$ easily forms associated molecules, the same being undoubtedly true of the compound $COPhBr,AlBr_3$, and these associated molecules are notably more active than the unassociated molecules. The reaction (3) in carbon disulphide solution may be considered as bimolecular, with a fall in the value of K, an excess of aluminium bromide again causing an enormous increase in the velocity of reaction. The velocity constant also increases slightly with an increase in the concentration of the benzene. W. G.

Preparation of Triarylmethane Dyes, Fast to Light. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 295495; from *Chem. Zentr.*, 1917, i, 150).—"Diarylindyl-dyes, which contain an amino-, sulpho-, alkyloxy- or acyloxy-group in place of the halogen atom in the para-position with regard to the methane carbon atom, are treated with primary aromatic amines."

The following intermediate compounds are mentioned: p-*methoxy*-p′-*dimethylaminobenzophenone*, m. p. 133°, from p-methoxybenzanilide and dimethylaniline; p-*hydroxy*-p′-*diethylaminobenzophenone*, m. p. 188°, from *p*-amino-*p*′-diethylaminobenzophenone, which is obtained from the nitro-compound, and this from *p*-nitrobenzanilide and diethylaniline; p-*dimethylaminobenzophenone*-p′-*sulphonic acid*, from the above amine by diazotisation, treatment with sulphurous acid and copper paste, and oxidation of the sulphinic acid with permanganate; p-*amino*-p′-*dimethylamino*-o′-*methylbenzophenone*, m. p. 151°, by the reduction of the

product obtained from *p*-nitrobenzanilide and dimethyl-*m*-toluidine; 1-*benzyl-2-methylindole*, b. p. 245°/16 mm., by melting the phenylbenzylhydrazone of acetone with zinc chloride.

J. C. W.

The Condensation of Aldehydes with ω-Bromoacetophenone, and some of the Compounds obtained thereby. SVEN BODFORSS (*Ber.*, 1918, **51**, 192—214. Compare A., 1917, i, 223).—When ω-bromoacetophenone is treated with a solution of sodium ethoxide, it yields the *cis*- and *trans*-modifications of 2-bromo-3:4-oxido-3:5-diphenyltetrahydrofuran (A., 1913, i, 1219), but if certain aldehydes are present, condensation between the unlike molecules takes place, resulting in the formation of ethylene oxides, most probably according to the scheme $COPh{\cdot}CH_2Br +$ $CHPhO = COPh{\cdot}CHBr{\cdot}CHPh{\cdot}OH = COPh{\cdot}CH{<}\genfrac{}{}{0pt}{}{CHPh}{O}{>} + HBr$. This condensation takes place particularly well if the aldehyde contains negative substituents, but negative results are usually given by aldehydes with positive substituents; thus, benzaldehyde, the nitrobenzaldehydes, *p*-chlorobenzaldehyde, bromo- and nitro-anisaldehydes, bromopiperonaldehyde, *m*-nitrocinnamaldehyde, cuminaldehyde, and terephthalaldehyde do react, whilst acetaldehyde, *iso*butaldehyde, heptaldehyde, citraldehyde, anisaldehyde, piperonaldehyde, cinnamaldehyde, and *p*-tolualdehyde do not react with ω-bromoacetophenone. ω-Chloro-*p*-methoxyacetophenone, however, is of itself so very stable towards sodium ethoxide that even an aldehyde like anisaldehyde will condense with it in the above manner, although only slowly.

The following are new examples of the condensation of aldehydes with ω-bromoacetophenone in equimolecular proportions: *o*-nitrobenzaldehyde gives *benzoyl-o-nitrophenylethylene oxide*, rectangular prisms, m. p. 110°, and thin needles, m. p. 175° (modifications "α" and "β"); bromoanisaldehyde forms *benzoyl-3-bromo-4-methoxyphenylethylene oxide*, very long needles, m. p. 158°; nitroanisaldehyde yields *benzoyl-3-nitro-4-methoxyphenylethylene oxide*, short prisms, m. p. 172—173°; bromopiperonaldehyde gives *benzoyl-(?)-bromo-3:4-methylenedioxyphenylethylene oxide*, needles, m. p. 98—98·5°; *m*-nitrocinnamaldehyde produces *benzoyl-m-nitrostyrylethylene oxide*,

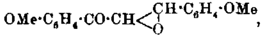
$$COPh{\cdot}CH{<}\genfrac{}{}{0pt}{}{CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2}{O}{>},$$

yellow crystals, m. p. 115—116°; terephthalaldehyde forms *benzoyl-p-aldehydophenylethylene oxide*, m. p. 116—119°.

Under the same conditions, benzoylacetone forms *α-acetyl-αβ-dibenzoylethane* (*acetyldiphenacyl*) in colourless cubes, m. p. 88—89°, which may be hydrolysed to diphenacyl, thus:

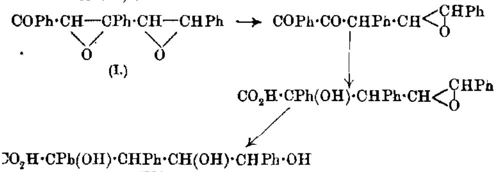
$$CHAc{:}CPh{\cdot}ONa + COPh{\cdot}CH_2Br \longrightarrow CHAcBz{\cdot}CH_2Bz \xrightarrow{NaOH}$$
$$CH_2Bz{\cdot}CH_2Bz + Ac{\cdot}ONa.$$

p-Chloroacetylanisole (ω-chloro-*p*-methoxyacetophenone) and anisaldehyde react to form *anisoylanisylethylene oxide*,



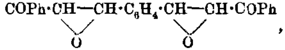
glistening, rhombic scales, m. p. 118—119°.

As has been mentioned already (*loc. cit.*), these ethylene oxides may be condensed with a further proportion of ω-bromoacetophenone to form dioxides. Thus, benzaldehyde may be converted into *a-benzoyl-βδ-diphenylbutadiene dioxide* (I), which crystallises in long needles, m. p. 156°. When boiled with aqueous-alcoholic potassium hydroxide, this dioxide yields *aγδ-trihydroxy-aβδ-triphenyl*-n-*valeric acid* (II), m. p. 178—179°, which forms a *tribenzoate*, m. p. 150—150·5°. The reaction apparently follows the course indicated, thus:



(II.)

A different type of dioxide is obtained by condensing a dialdehyde with a bimolecular quantity of ω-bromoacetophenone. Thus, terephthalaldehyde gives *phenylenebisdibenzoylethylene oxide*,

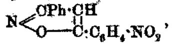


which crystallises in thin, pearly scales, m. p. 220—222°, and may be reduced by potassium iodide in glacial acetic acid to terephthalylidenediacetophenone, $C_6H_4(CH{:}CH{\cdot}COPh)_2$, the product being identical with that obtained by the condensation of acetophenone with telephthalaldehyde (see Lendenfeld, A., 1907, i, 221).

Benzoyl-*m*-nitrophenylethylene oxide reacts with stannic chloride as though it were a diketone, but the *product*, $C_{15}H_{11}O_4N,SnCl_4$, crystallising in large, yellowish-brown groups, is not identical with that given by the genuine diketonic isomeride,

$$COPh{\cdot}CO{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2.$$

Widman has shown that benzoylphenylethylene oxide reacts with hydroxylamine under different conditions to form various compounds, partly oximes and partly cyclic substances (A., 1917, i, 221). Benzoyl-*m*-nitrophenylethylene oxide gives equally complicated reactions. When boiled with hydroxylamine hydrochloride and alcohol, it yields 3-*phenyl*-5-m-*nitrophenylisooxazole*,



in thin tablets, m. p. 176—177°, which may also be prepared in the same way from the isomeric phenyl *m*-nitro-α-hydroxystyryl ketone (*loc. cit.*, 224). The mother liquor from this contains an *oxime*, "α," m. p. 121·5°, which is soluble in sodium hydroxide and non-reducible by hydriodic acid, and gives an *acetate*, large flakes, m. p. 132—132·5°. If the ethylene oxide is boiled with hydroxylamine hydrochloride and sodium acetate in alcohol, it yields another *oxime*, "β," which crystallises in slender needles, m. p. 145°, forms an *acetate*, prisms, m. p. 123°, changes into the α-oxime when treated with hydrochloric acid, and into a third *oxime*, "γ," small, glassy cubes, m. p. 153°, when crystallised from methyl alcohol, and produces 4- or *5-hydroxy-3-phenyl-5-*m*-nitrophenyliso-oxazolidine*,

$$NH<\begin{matrix}CHPh\cdot CH\cdot OH\\ O\text{———}CH\cdot C_6H_4\cdot NO_2\end{matrix} \quad \text{or} \quad NH<\begin{matrix}CHPh\cdot CH_2\\ O\text{———}C(OH)\cdot C_6H_4\cdot NO_2\end{matrix},$$

prisms, m. p. 145—146° (*nitroso*-compound, m. p. 135—140°), when boiled with potassium iodide and glacial acetic acid.

Benzoyl-*m*-nitrophenylethylene oxide reacts with semicarbazide acetate in cold alcohol to form *4-hydroxy-3-phenyl-5-*m*-nitrophenyl-4:5-dihydropyrazole-1-carboxylamide*,

$$NH_2\cdot CO\cdot N<\begin{matrix}CH(C_6H_4\cdot NO_2)\cdot CH\cdot OH\\ N\text{=========}CPh\end{matrix},$$

which crystallises in short prisms, m. p. 162—163° (decomp.). The same compound is given by the corresponding chlorohydrin, $OH\cdot CHBz\cdot CHCl\cdot C_6H_4\cdot NO_2$, but the isomeric phenyl *m*-nitro-α-hydroxystyryl ketone yields a different product, namely, the normal *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N\colon CPh\cdot CH\colon C(OH)\cdot C_6H_4\cdot NO_2$, m. p. 120—125° (decomp.). Similarly, the chlorohydrin usually reacts with hydrazine hydrate to form *4-hydroxy-3-phenyl-5-*m*-nitrophenyl-4:5-dihydropyrazole*, in rhombic leaflets, m. p. 184—185°, but on one occasion *4-hydroxy-5-hydrazino-3-phenyl-5-*m*-nitrophenyl-4:5-dihydropyrazole* was obtained instead, in yellow needles, m. p. 165°.

Thiocyanic acid and thiocarbamides also condense with benzoyl-*m*-nitrophenylethylene oxide, water being eliminated. Thiocyanic acid gives a *compound* which crystallises in pale yellow prisms, m. p. 120—125° (decomp.), forms an *acetyl* derivative, m. p. 111°, and is probably represented by the formula

$$CO<\begin{matrix}NH\cdot CHBz\\ S\text{——}CH\cdot C_6H_4\cdot NO_2\end{matrix}.$$

Thiocarbamide gives a deep yellow *product*, m. p. 176—177° (decomp.), to which the alternative formulæ,

$$NH\colon C<\begin{matrix}NH\cdot CHBz\\ S\text{——}CH\cdot C_6H_4\cdot NO_2\end{matrix} \quad \text{or} \quad NH\colon C<\begin{matrix}NH\cdot CH\cdot C_6H_4\cdot NO_2\\ S\text{——}CHBz\end{matrix},$$

are assigned. Thiocarbanilide forms a yellow *product*, m. p. 221° (decomp.), which would be the diphenyl derivative of the foregoing substance. It gives unstable additive compounds with bromine

and iodine, and is converted by boiling with sodium ethoxide solution into an orange-red *isomeride*, m. p. 245°. J. C. W.

Action of Light on Keto-oxido-compounds. SVEN BODFORSS (*Ber.*, 1918, **51**, 214—219).—Benzoylphenylethylene oxide, benzoyl-*m*-nitrophenylethylene oxide, and benzoyl-*p*-chlorophenylethylene oxide undergo rearrangement into phenyl α-hydroxystyryl ketones with increasing readiness when their methyl-alcoholic solutions are exposed to the light of a mercury lamp. The yields of the isomerides are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can eventually be isolated.

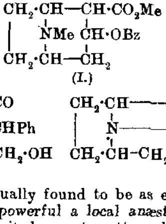
The production of phenyl *m*-nitro-α-hydroxystyryl ketone by another method has already been described (A., 1917, i, 224). A third method consists in the action of *m*-nitrobenzoyl chloride on benzoylacetone in the presence of sodium ethoxide, followed by hydrolysis of the acetyl derivative by boiling hydrochloric acid. *Phenyl* p-*chloro-α-hydroxystyryl ketone*, $COPh{\cdot}CH{:}C(OH){\cdot}C_6H_4Cl$, very pale yellow crystals, m. p. 89°, is also prepared as follows: *p*-chlorobenzylideneacetophenone is treated with bromine, when two isomeric *dibromides*, $COPh{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4Cl$, are formed, a sparingly soluble one, m. p. 178—180°, decomp. 190—193°, and a freely soluble one, m. p. 125—126°, decomp. 142—143°, either of which gives the desired keto-enol on boiling with alcoholic potassium hydroxide. J. C. W.

Action of Hydriodic Acid on Cinchonine and its Isomerides. Cinchoniline, Cinchonigine, and *apo*Cinchonine. E. LÉGER (*Compt. rend.*, 1918, **166**, 469—472. Compare this vol., i, 121).—When heated with hydriodic acid, cinchonine and cinchoniline give the same hydriodocinchonine, whilst cinchonigine and *apo*cinchonine give an isomeric *hydriodo*apo*cinchonine*, as shown by a study of the optical activity of the dihydrochlorides and dinitrates of the four hydriodo-derivatives. W. G.

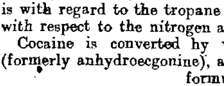
Preparation of Histidine. HARRY M. JONES (*J. Biol. Chem.*, 1918, **33**, 429—431).—Two litres of hydrochloric acid are added to an equal volume of the concentrated suspension of red blood corpuscles obtained by centrifugalising defibrinated ox blood. The mixture is boiled on a sand-bath for eighteen hours, or until the biuret reaction is negative. After exactly neutralising by the addition of about an equal volume of saturated sodium carbonate solution, the mixture is filtered, and ammonia removed from the filtrate by boiling for an hour with 25 grams or more of sodium hydroxide. On cooling, leucine and tyrosine are deposited, and should be filtered off. The histidine is now precipitated by the alternate addition of concentrated solutions of mercuric chloride and sodium carbonate until a filtered portion no longer gives a voluminous precipitate with the mercuric chloride solution. The precipitate is collected, washed, suspended in five times its volume

of water, and, using hydrochloric acid, the latter rendered acid to bromophenol-blue ($p_H = 3$). The mercury-histidine compound dissolves, and, after filtration, is reprecipitated by sodium carbonate. It is finally suspended in water and the histidine liberated by hydrogen sulphide. After filtration, the filtrate is concentrated at the ordinary temperature, whereon large, yellow crystals of histidine hydrochloride separate from the brown, syrupy mother liquor. The yield is about 15 grams. H. W. B.

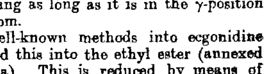
Conversion of Cocaine into New, Physiologically Active Substances. J. von Braun and E. Müller (*Ber.*, 1918, **51**, 235—252).—Von Braun has begun an inquiry into the interesting question of the influence on physiological activity of displacing some specific group or other from one position to another in the molecule of an active drug. So far, he has experimented on codeine (A., 1916, i, 665; 1917, i, 163), but this is not quite a suitable material, as its constitution is still not definitely known. The problem has now been attacked in the group of the tropeines, in which the presence of an acylated hydroxyl group in the γ-position with regard to the basic nitrogen atom may be regarded as the factor controlling the physiological behaviour. The question raised, therefore, in this paper is what is the effect of displacing the hydroxyl group to another part of the molecule, still in the γ-position with regard to the nitrogen atom? Cocaine (I) has been converted into two such compounds, II and III.



(I.)



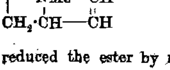
(II.)



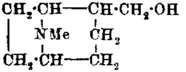
(III.)

Compound II is actually found to be as effective a mydriatic as atropine, and III as powerful a local anæsthetic as cocaine. It follows, therefore, that it does not matter where the acyloxy-group is with regard to the tropane ring as long as it is in the γ-position with respect to the nitrogen atom.

Cocaine is converted by well-known methods into ecgonidine (formerly anhydroecgonine), and this into the ethyl ester (annexed formula). This is reduced by means of hydrogen and palladium to *ethyl dihydroecgonidine*, b. p. 127—129°/12 mm., which forms an *aurichloride*, yellow leaflets, m. p. 167°, and a *methiodide*, long needles, m. p. 219°. Willstätter (A., 1897, i, 385) reduced the ester by means of sodium and amyl alcohol; his pro-

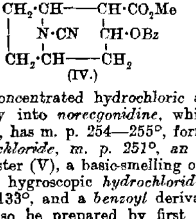


duct had the same b. p., but gave quite different salts, and it is fairly obvious that transformation about the asymmetric carbon atom had occurred to a considerable extent in his experiment. The next stage consists in reducing the ester by means of sodium and alcohol to the hydramine, and Willstätter's product gives the same result as the above. The new base, *homotropine* (annexed formula), crystallises in needles, m. p. 85°, $[\alpha]_D^{20}$ +22·48° (in alcohol), and forms a *hydrochloride*, m. p. 192°, an *aurichloride*, m. p. 191°, a *picrate*, thin needles, m. p. 208—209°, and a *methiodide*, which may be converted into a

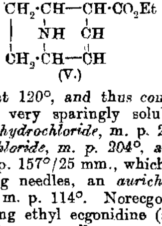


platinichloride, m. p. 183°, and an *aurichloride*, yellow leaflets, m. p. 238°. The *benzoate* is produced by means of benzoyl chloride; it is a viscous oil, which forms a *platinichloride*, m. p. 201°, an *aurichloride*, m. p. 161°, and a lemon-yellow *picrate*, m. p. 177°. *Homotropine tropate* (II) is prepared by warming the hydrochloride with acetyltropyl chloride, hydrolysing the product by warm water to remove the acetyl group, and adding dilute sodium hydroxide to the solution; it is obtained as an oil, which forms a *platinichloride*, m. p. 192°. The oily *mandelate* and its *platinichloride*, m. p. 192°, are formed in the same way.

For the preparation of the other compound (III), cocaine is first treated with cyanogen bromide in warm chloroform, when *cyanonorcocaine* (IV), m. p. 123—124°, is produced. This is heated



(IV.)



(V.)

with concentrated hydrochloric acid at 120°, and thus converted directly into *norecgonidine*, which is very sparingly soluble in alcohol, has m. p. 254—255°, forms a *hydrochloride*, m. p. 257°, a *platinichloride*, m. p. 251°, an *aurichloride*, m. p. 204°, and an *ethyl* ester (V), a basic-smelling oil, b. p. 157°/25 mm., which gives a very hygroscopic *hydrochloride*, long needles, an *aurichloride*, m. p. 133°, and a *benzoyl* derivative, m. p. 114°. Norecgonidine may also be prepared by first treating ethyl ecgonidine (above) with cyanogen bromide, but the yield is very small, rupture of the tropane ring being the main result. The ester V is hydrogenated in the presence of palladium, giving *ethyl dihydronorecgonidine*, b. p. 135—137°/19 mm., D_4^{19} 1·0856, $[\alpha]_D^{19}$ +5·881°, which yields a hygroscopic *hydrochloride*, m. p. 149—150°, and an *aurichloride*, m. p. 110°. The *N-γ-benzoyloxypropyl* derivative (III) is prepared by the action of γ-bromopropyl benzoate (compare A., 1916, i, 631); it is an oil which forms a *hydrochloride*, long needles, m. p. 142°, a *platinichloride*, m. p. 94—95°, and an *aurichloride*, m. p. 127—128°.

Another interesting product is obtained by the action of γ-bromopropyl benzoate on the ester V. It is designated *eccaine*, and is

an oil which forms a *hydrochloride*, m. p. 117°, a *picrate*, m. p. 139—141°, and a *methiodide*, m. p. 194—195°. It is more active as an anæsthetic than cocaine, is non-toxic, and so stable that its solutions may be sterilised easily. J. C. W.

Preparation of Homotropine. CHEMISCHE WERKE, GRENZACH (D.R.-P., 296742; from *Chem. Zentr.*, 1917, i, 612).—Compare preceding abstract. J. C. W.

Preparation of *N*-Demethylated Derivatives of the Alkaloids of the Cocaine and Atropine Groups, their Derivatives and Salts. CHEMISCHE WERKE, GRENZACH (D.R.-P., 301870; from *Chem. Zentr.*, 1918, i, 250).—Compare von Braun and Müller (above). Acetyltropine reacts with cyanogen bromide to give *acetylcyanonortropine*, m. p. 96°, which yields nortropine on boiling with moderately concentrated hydrochloric acid.
J. C. W.

Production of Derivatives of Homotropine. CHEMISCHE WERKE, GRENZACH (D.R.-P., 299806; from *Chem. Zentr.*, 1917, ii, 510).—The pharmacologically inactive homotropine can be rendered active by esterification with organic acids such as benzoic, tropic, or mandelic acid, the resulting esters (see von Braun and Muller, preceding page) resembling atropine in their effect on the animal organism. In this way, anhydroecgonine, hitherto valueless, can be converted into therapeutically useful products.
D. F. T.

New Cases of Isomerism in the Isatin Series. GUSTAV HELLER [with FRITZ BAUMGARTEN] (*Ber.*, 1918, **51**, 180—190. Compare A., 1917, i, 219).—The discovery of three different forms of isatin, or at least ethers of three forms, has led the author to examine 5:7-dimethylisatin, with the surprising and so far inexplicable result that no fewer than four individual isomerides have been obtained. These are numbered I, II, III, and IV, for the time being, in the order of their discovery.

Isomeride I.—This is the normal product, $C_6H_2Me_2<^{CO}_{NH}>CO$, obtained originally from dichloroacetic acid and 1:3:4-xylidine (A., 1908, i, 218). It crystallises in yellow needles, m. p. 243°, and forms a greyish-red N-*silver* salt, from which 1:5:7-*trimethylisatin* may be obtained, in dark red leaflets, m. p. 214°, this yielding a yellow *phenylhydrazone*, m. p. 161°. The sodium salt of the isatin reacts with silver nitrate to form a very dark brown O-*silver* salt, $C_6H_2Me_2<^{CO}_{N}\gg C\cdot OAg$, but this yields the original isatin on acidification or treatment with methyl iodide, and not the lactim modification or its methyl ether.

Isomeride II.—This is produced by the action of benzoyl chloride on the above *N*-silver salt, suspended in warm benzene. It crystallises in large, dark red, oblique prisms, m. p. 204° (decomp.); it gives the indophenin reaction at once, whereas the colour only develops slowly with isomeride I; it dissolves in pure sulphuric acid with dark violet colour, whereas isomeride I gives a ruby-red solution; it is insoluble in sodium hydroxide solution; it forms a *phenylhydrazone*, which is fairly soluble in alcohol and crystallises in yellow needles, m. p. 216° (decomp.), whereas the phenylhydrazone of isomeride I is very sparingly soluble and has m. p. 272°; and it reacts with methyl sulphate, which isomeride I does not, giving a *methyl ether*, quadratic, red tablets, m. p. 247° (decomp.), which forms a yellowish-red *phenylhydrazone*, m. p. 203°. These reactions serve to establish the fact that the second isomeride is a distinct individual, but that it is neither the lactim modification nor the expected isatol, that is, neither

$$C_6H_2Me_2{<}{}^{CO}_{N}{\gg}C{\cdot}OH \quad \text{nor} \quad C_6H_2Me_2{<}{}^{C(OH)}_{N}{>}CO.$$

Isomeride III.—This is formed by triturating isomeride II with dilute sodium hydroxide, when a red, sparingly soluble sodium salt is produced, which is acidified. It crystallises in bluish-red, rectangular prisms, m. p. 279°; it yields the same sodium salt when mixed with sodium hydroxide, but if the suspension is kept, the colour fades and the isomeride I may be recovered on acidifying; it is freely soluble in dilute sodium carbonate or ammonia; it does not give the indophenin reaction, and its solution in concentrated sulphuric acid is only faintly reddish-yellow; it does not give a phenylhydrazone; it forms a bluish-red *silver* salt; and it may be converted, through the sodium or silver salts, or by means of diazomethane, into a *methyl ether*, yellowish-red tablets, m. p. 210°, insoluble in warm, dilute alkali hydroxides. This modification therefore conforms to the type of isatol.

Isomeride IV.—This is produced when isomeride III is crystallised from hot acetic acid. It has m. p. 267°, forms a readily hydrolysable, colourless sulphate, dissolves in alcoholic potassium hydroxide, does not yield a phenylhydrazone, and reacts with diazomethane to form a *methyl ether*, fiery-red, glistening, flat prisms, m. p. 211°, which depresses the m. p. of the methyl derivative of isomeride III. The compound is therefore another isatol.

There are, apparently, two pairs of structurally similar isomerides, I and II being of the normal isatin type and III and IV of the isatol series, but I and III resemble each other in their acidic properties and II and IV in their neutral or basic properties.

J. C. W.

***Bz*-Hydroxyindolinones [Hydroxyoxindoles].** GEORG WAHL (*Monatsh.*, 1918, **39**, 525—535).—No oxindole has hitherto been prepared containing a hydroxyl group in the benzene nucleus. By extending the indolinone synthesis, based on the

elimination of ammonia from aliphatic phenylhydrazides (Brunner, A., 1897, i, 100), to the corresponding anisylhydrazides, it is possible to obtain 5-methoxyoxindole derivatives. Thus, iso*butyryl* p-*anisylhydrazide*, colourless leaflets or granules, m. p. 142°, when heated with lime at approximately 180° for about two hours, yields 5-*methoxy*-3 : 3-*dimethyloxindole*, $\begin{matrix}CMe_2—CO\\ C_6H_3(OMe)\end{matrix}>NH$, rhombic tablets, m. p. 150° (*bromo*-derivative $C_{11}H_{12}O_2NBr$, colourless needles, m. p. 218°; *acetyl* derivative, needles, m. p. 84°; *benzoyl* derivative, needles, m. p. 82°; *silver* salt, very unstable, greenish-white, gelatinous mass), accompanied by a little *iso*butyrylamide, leaflets, m. p. 124°. By treating with boiling hydriodic acid for one hour, the methoxyl compound is converted into 5-*hydroxy*-3 : 3-*dimethyloxindole*, $\begin{matrix}CMe_2—CO\\ C_6H_3(OH)\end{matrix}>NH$, colourless needles, m. p. 244°; *diacetyl* derivative, colourless needles, m. p. 126°; *benzoyl* derivative, $C_{17}H_{15}O_3N$, needles, m. p. 240°. In a similar manner, iso*butyryl* o-*anisylhydrazide*, m. p. 120°, when heated with lime, is converted into 7-*methoxy*-3 : 3-*dimethyloxindole*, $C_{11}H_{13}O_2N$, colourless needles, m. p. 101° (*bromo*-derivative, $C_{11}H_{12}O_2NBr$, colourless needles, m. p. 200°), which is demethylated by hydriodic acid with formation of 7-*hydroxy*-3 : 3-*dimethyloxindole*, $C_{10}H_{11}O_2N$, m. p. 250°. D. F. T.

Selenomethylene-blue. P. Karrer (*Ber.*, 1918, **51**, 190—192).—In his account of some new selenazine dyes, the author showed that the true selenium analogue of methylene-blue had not yet been described, references to such a dye being erroneous (A., 1916, i, 434). The compound is easily prepared by Kehrmann's method (*ibid.*, 435). Selenodiphenylamine is treated with bromine in glacial acetic acid until phenazselenonium perbromide is completely precipitated, in brightly shimmering, brown flakes, and this is triturated with an alcoholic solution of dimethylamine. 3 : 6-*Tetramethyldiaminophenazselenonium bromide* (*selenomethylene-blue bromide*), $NMe_2\cdot C_6H_3\lessgtr\begin{matrix}N\\ SeBr\end{matrix}>C_6H_3\cdot NMe_2$, is formed, and, after crystallisation from boiling water, is obtained in shimmering needles with metallic green reflex, possessing the same stability and tinctorial properties as methylene-blue. J. C. W.

Action of Aniline on Carbon Tetrachloride. Ernst Johannes Hartung (T., 1918, **113**, 163—168).—In 1858, Hofmann showed that carbon tetrachloride and aniline react at 180° to form pararosaniline and diphenylaminobenzamidine,

$$NHPh\cdot C(NPh)\cdot C_6H_4\cdot NH_2.$$

This reaction has now been studied at lower temperatures and in the presence of a copper–mercury couple as a catalyst.

The two liquids react even at the ordinary temperature. Brown discolorations soon appear, but the first definite product, after

some weeks' action, seems to be *s*-diphenylcarbamide. The production of this can be traced to the action of moisture on a dichloro-compound, $CCl_2(NHPh)_2$. After some months, diphenylaminobenzamidine separates. The by-products vary according to the proportions of the reagents employed. With a very large excess of carbon tetrachloride, a compound which crystallises in small, reddish-brown prisms, m. p. 245° (corr.), and a dark blue dye separate, as well as diphenylcarbamide, during the early months.

In the presence of amalgamated copper, the mixtures solidify within a few days, diphenylaminobenzamidine hydrochloride being the chief product, accompanied by azobenzene, phenylcarbylamine, and a little pararosaniline. The reaction is still more rapid at 80—90°, but is never complete, and many obscure by-products are formed.

Diphenylaminobenzamidine hydrochloride becomes yellow on rubbing, but reverts to white after some days. These changes can be induced repeatedly. J. C. W.

Reactions of the Formamidines. VII. The Constitution of some Pyrazole Derivatives. F. B. DAINS and ROLLA N. HARGER (*J. Amer. Chem. Soc.*, 1918, **40**, 562—569. Compare A., 1902, i, 602; 1906, i, 781; 1913, i, 1086, 1096; 1916, i, 676).—It has already been shown that the substituted formamidines react with compounds containing methylene hydrogen, giving rise to products in which the $-CH_2-$ group is replaced by the grouping $:CH\cdot NHR$. By the action of hydrazine on amino-methylene derivatives of ethyl acetoacetate, it is now found that derivatives of 5-methylpyrazole-4-carboxylic acid can be obtained.

m-*Bromoanilinomethyleneacetoacetanilide*,

$$NHPh\cdot CO\cdot CAc:CH\cdot NH\cdot C_6H_4Br,$$

yellowish-white needles, m. p. 113°, prepared by the interaction of *m*-dibromodiphenylformamidine and acetoacetanilide or aceto-*p*-toluidide, reacts with hydrazine in alcoholic solution, yielding 5-*methylpyrazole-4-carboxyanilide*, $\begin{matrix} N{=\!=}CH \\ | \\ NH\cdot CMe \end{matrix}\!\!>\!C\cdot CO\cdot NHPh$, needles, m. p. 179°, the same substance also being obtained by the action of hydrazine on anilinomethyleneaceto-*p*-toluidide, the reaction product of acetoaceto-*p*-toluidide and diphenylformamidine. When heated together at 120—130°, ethyl acetoacetate and *o*-phenetidine undergo condensation, with formation of *acetoaceto-o-phenetidide*, $CH_2Ac\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, needles, m. p. 92°, which is capable of reacting with diphenylformamidine, with formation of *anilinomethyleneacetoaceto-o-phenetidide*,

$$NHPh\cdot CH:CAc\cdot CO\cdot NH\cdot C_6H_4\cdot OEt,$$

needles, m. p. 135°; hydrazine or hydrazine hydrate converts this into 5-*methylpyrazole-4-carboxy-o-phenetidide*,

$$\begin{matrix} N{=\!=}CH \\ | \\ NH\cdot CMe \end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot C_6H_4\cdot OEt,$$

needles, m. p. 163°; *hydrochloride*, m. p. 200° (decomp.). At

100°, ethyl acetoacetate reacts with di-*o*-phenetidylformamidine, giving *ethyl* o-*phenetidinomethyleneacetoacetate*, $C_{15}H_{19}O_4N$, colourless crystals, m. p. 111°, which on treatment in hot alcoholic solution with hydrazine hydrate yields *ethyl* 5-*methylpyrazole*-4-*carboxylate*, $\begin{matrix} N{=}CH \\ NH\cdot CMe \end{matrix}>C\cdot CO_2Et$, needles with $1H_2O$, m. p. 46°, or m. p. 54° when anhydrous.

Phenylhydrazine reacts with anilinomethyleneacetylacetone, giving rise to 4-acetyl-1-phenyl-5-methylpyrazole, in agreement with Claisen's results (A., 1897, i, 441), but with ψ-cumidinomethyleneacetylacetone and *p*-toluidinomethyleneacetylacetone, this product is accompanied by the *phenylhydrazone*, yellow needles, m. p. 175°, of the acetylphenylmethylpyrazole. The reaction product of acetylphenylmethylpyrazole and hydrazine hydrate in alcoholic solution is the corresponding *hydrazone*, $\begin{matrix} N{=}CH \\ NPh\cdot CMe \end{matrix}>C\cdot CMe{:}N\cdot NH_2$, four-sided prisms, m. p. 94·5° (*hydrochloride*, m. p. 218°; *benzylidene* derivative, $C_{10}H_9N_2\cdot CMe{:}N\cdot N{:}CHPh$, yellow crystals, m. p. 127°), which when warmed with a little formic or acetic acid in ethyl acetate solution undergoes intermolecular condensation, with formation of hydrazine and *bis*-4-*acetyl*-1-*phenyl*-5-*methylpyrazolylazine*, $N_2({:}CMe\cdot C_{10}H_9N_2)_2$, yellow crystals, m. p. 174°; this, on boiling with hydrochloric acid, regenerates the original pyrazole compound. When *o*-phenetidinomethyleneacetylacetone and hydrazine hydrate are warmed together in alcoholic solution, a yellow compound, m. p. 320°, is obtained; this has already been described by Gaugler and by J. Gattermann (*Diss.*, Freiburg, 1903 and 1904), who regarded it as the triazine, $\begin{matrix} CH{=}C\cdot CMe{:}N \\ CH_2\cdot C{:}N{-}NH \end{matrix}$, but a more probable constitution is that of the azine derivative of 4-acetyl-5-methylpyrazole.

During the course of the investigation, *acetoaceto*-m-*bromoanilide*, $CH_2Ac\cdot CO\cdot NH\cdot C_6H_4Br$, plates, m. p. 83°, and m-*bromoanilinomethyleneacetoaceto*-m-*bromoanilide*,

$$C_6H_4Br\cdot NH\cdot CO\cdot CAc{:}CH\cdot NH\cdot C_6H_4Br,$$

pale yellow needles, m. p. 154°, were prepared, the latter by the interaction of ethyl acetoacetate and di-*m*-bromodiphenylformamidine. It was also found that the benzoyl derivative of *m*-bromoaniline has m. p. 135—136° instead of 120°, as stated earlier (Kottenhahn, A., 1891, 1237). The results of the investigation demonstrate that the reaction products of hydrazine or phenylhydrazine and arylaminomethyleneacetoacetarylamides are pyrazole compounds, and not pyrazolone derivatives, as has been assumed earlier (Ruggeburg, *Diss.*, Freiburg, 1903; J. Gattermann, *Diss.*, 1904). D. F. T.

Preparation of Mono-azo-dyes suitable for the Manufacture of Pigments. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 297414; from *Chem. Zentr.*, 1917, i, 981—982).—In place of 1-benzoylamino-7-hydroxynaphthalene, or derivatives of

this containing substituents in the benzoyl radicle, the corresponding *N*-alkyl compounds can be used. 1-Benzoylethylamino-7-hydroxynaphthalene, 1-benzoylmethylamino-7-hydroxynaphthalene, and 1 : 2′-chlorobenzoylethylamino-7-hydroxynaphthalene have m. p. 224—225°, 186—187°, and 232—233° respectively.

D. F. T.

Structure of Yeast-nucleic Acid. III. Ammonia Hydrolysis. P. A. LEVENE (*J. Biol. Chem.*, 1918, **33**, 425—428. Compare this vol., i, 130).—Uridinephosphoric acid can be isolated from the products of the hydrolysis of yeast-nucleic acid by dilute ammonia at 115° through the intermediate formation of the mixed brucine salts of the cytosine and uracil nucleotides, which, after separation, are converted into the barium salts, as previously described (*loc. cit.*). H. W. B.

Effects of Electrolytes on Gelatin and their Biological Significance. II. Effect of Salts on the Precipitation of Acid and Alkali-gelatin by Alcohol. Antagonism. W. O. FENN (*J. Biol. Chem.*, 1918, **33**, 439—451. Compare this vol., i, 198).—Employing the technique previously described, the author finds that the effect of combinations of salts with acids and alkalis on the precipitability of the gelatin by alcohol is greater or less than the effect produced by the acid or alkali alone, according to the valency of the ions in the salt. Thus, salts with univalent ions (like sodium chloride) decrease the effect of both acids and alkalis on the precipitability of gelatin. Salts with bivalent or tervalent ions (like calcium or aluminium chloride) decrease the effect of alkalis on gelatin, but increase the effect of acid, except in high concentrations of salt or acid, where the effect is decreased. Salts with bivalent or tervalent anions (like sodium sulphate or citrate) decrease the effect of acids on gelatin, but increase the effect of alkalis, except at high concentration, when the greater the concentration of either salt or alkali, the less the alcohol necessary for precipitation. These results are comparable and in some respects analogous to the antagonistic effects of various electrolytes observed in certain biological phenomena (compare Loeb, A., 1916, i, 186, and this vol., i, 51). H. W. B.

Ionisation of Proteins and Antagonistic Salt Action. JACQUES LOEB (*J. Biol. Chem.*, 1918, **33**, 531—549. Compare A., 1917, ii, 453, and Fenn, preceding abstract).—The author describes a new method of studying the effect of neutral salts on gelatin in which the powdered protein is treated with the salt in a concentration of *M*/4 or *M*/8, and then the excess of salt is removed by washing with water or with a weak solution of another salt. In these circumstances, the initial swelling occurring in *M*/8-sodium chloride is greatly increased by perfusion with water or a weak solution of a neutral salt with a univalent metal. The additional swelling is only possible as long as the weaker solution remains below a certain concentration, and it is found that the limiting

molecular concentration which will cause the additional swelling is twice as great if the anion is univalent as when it is bivalent, regardless of the nature of the anion and cation. The influence of neutral salts on the swelling of gelatin is therefore of a stoicheiometric order, and the inhibiting action of a salt on the additional swelling is explained by the author as being due to a diminution of the degree of electrolytic dissociation of a metal–protein compound first produced. Thus, neutral salts with a univalent cation like sodium chloride in concentrations of $M/8$ or $M/4$ form highly ionisable salts with gelatin. On treatment with water, dissociation occurs into positively charged metal ions and negative gelatin ions, which may or may not contain the anion of the salt in non-dissociated bondage. It is the formation of these gelatin ions that causes the additional swelling observed. The metals of the alkaline earth group form salts with gelatin which are not capable of swelling and do not ionise. The transformation of gelatin salts with univalent cation (capable of swelling) into gelatin salts with bivalent cation (not capable of swelling) is the cause of the antagonistic action of the metals of the calcium group.

H. W. B

Physiological Chemistry.

The Presence of Hæmatin in Human Blood-serum. I. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **85**, 171—187).—As a result, chiefly of clinical experience, hæmatin could be detected as a pathological constituent of the blood after intoxication by the following substances: chromates, chlorates, carbon monoxide, various gases, resorcinol, mono-, di-, and tri-nitrobenzene, picric acid, acetanilide, exalgin, *p*-phenylenediamine, pyrodine (acetylphenylhydrazine), maretine, trional, trigemine, excessive use of tobacco.

S. B. S.

The Presence of Hæmatin in Human Blood-serum. II. JOH. FEIGL and RUD. DEUSSING (*Biochem. Zeitsch.*, 1918, **85**, 212—229).—This paper is chiefly of clinical interest, giving the results of the examination of the serum for the presence of hæmatin in about 700 cases. S. B. S.

Chemical Studies on Physiology and Pathology. II. Immunity Reactions. G. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **85**, 1—44. Compare this vol., i, 47).—A theoretical paper, in which the authors develop further their conceptions of the nature of proteins, which have been already the subject of numerous papers. They conceive the antibodies as derived from the antigen itself; this undergoes a partial degradation in the body, and the degraded but still specific product is then adsorbed by certain protein particles of the blood (derived from the degrada-

tion of cells and in the "globulin" stage). The complex thus formed has the property of adsorbing new quantities of antigen, thus giving rise to the known immunity reactions, such as precipitation, deintoxication, etc. The ideas thus expressed are developed in considerable detail. S. B. S.

Deaminisation and Carbamide Formation in the Animal Body. WILHELM LÖFFLER (*Biochem. Zeitsch.*, 1918, **85**, 230—294). —The surviving liver (rabbits and dogs) was perfused with Ringer's solution mixed with blood, and the ammonia and carbamide were estimated in the perfusing fluid both before and after perfusion. The carbamide was estimated by the urease method. It is shown that there is an increase in the carbamide after perfusion even when no nitrogen compound is added to the perfusion liquid. The addition of the ammonium salts of inorganic acids causes, however, a considerable addition to the amount of carbamide formed, leaving no doubt that the ammonium salts are converted into carbamide, and this happens even when the perfusing liquid is distinctly acid. Acids inhibit the formation of carbamide somewhat, without preventing it. Primary amines give rise to carbamide also when perfused through the liver, the lower amines, such as methylamine or ethylamine, being completely burnt, and the higher amines (amylamine, benzylamine, *p*-hydroxyaniline, and phenylethylamine) less completely. No substituted carbamides could be detected. Trimethylamine is completely demethylated in the liver, the ammonia being converted into carbamide. S. B. S.

Presence of the Co-ferment of the Alcoholic Yeast Fermentation in Muscular Tissue and its Significance in the Respiratory Mechanism. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **101**, 165—175).—The extracts of muscle and other tissues are prepared by boiling the minced tissue in an equal weight of water and filtering. Samples of yeast juice which have been inactivated by removal of the co-ferment by Harden and Young's method (A., 1907, i, 104) are reactivated by the addition of the tissue extract. The author finds that glycolysis by yeast or by muscle juice is similarly accelerated by the tissue extract (compare Harden and MacLean, A., 1911, ii, 215, 905). H. W. B.

The Synthesis of Luciferin. RAPHAEL DUBOIS (*Compt. rend.*, 1918, **166**, 578—580. Compare *ibid.*, 1917, **165**, 33, and Harvey, A., 1917, i, 365).—The author has extracted from *Pholade dactyle* a substance presenting all the characteristics of taurine, and also a luciferase which converts the taurine into luciferin. W. G.

[Physiological] Action of an Isomeride of Caffeine. WILLIAM SALANT and HELENE CONNET (*J. Pharm. Exper. Ther.*, 1918, **11**, 81—88).—The authors find that 2 : 8-dioxy-1 : 7 : 9-trimethyl-1 : 2 : 8 : 9-tetrahydropurine (Johns, A., 1914, ii, 922) is

much less active physiologically than the isomeric 2:6-dioxy-compound (caffeine), the relative toxicity for rabbits of the two substances being about 1:11. The new isomeride caused a moderate increase in the secretion of urine in some experiments, but it failed to stimulate renal activity in others. When tested on frogs, it was found to act as a weak cardiac stimulant. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

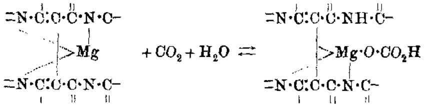
Disinfectant Action of Quinine Alkaloids on Pathogenic Bacteria. R. BIELING (*Biochem. Zeitsch.*, 1918, **85**, 188—211. Compare Schaeffer, this vol., i, 93).—The alkaloids investigated were quinine, optochine (ethylhydrocupreine), eucupine (*iso*amylhydrocupreine), and the *iso*octyl-, decyl-, and dodecyl-hydrocupreines. These have been found to have a specific disinfectant actiou on the bacilli of diphtheria, splenic fever, and tetanus. Eucupine and *iso*octylhydrocupreine are generally the most effective. S. B. S.

Influence of Acids on Germination. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1918, **166**, 547—552).—Mineral acids must be classed amongst those substances considered most injurious to germination. This toxic action may be modified by the presence of electrolytes in the form of salts, or by those that the acid may form by its action on the teguments of the seeds or the glass of the apparatus. Amongst these antitoxic substances, calcium appears to be one of the most powerful. W. G.

The Assimilation of Carbon Dioxide. III. Behaviour of Colloidal Chlorophyll towards Carbon Dioxide. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1917, **50**, 1791—1801. Compare this vol., i, 207).—Solutions of chlorophyll in organic solvents do not absorb more carbon dioxide than the pure liquids, but the hydrosols absorb much more of the gas than other colloidal solutions, the absorption reaching a maximum of two molecular proportions to every magnesium atom. The absorption is attended by the precipitation of phæophytin, and the reaction may consequently be represented, in the case of chlorophyll-*a*, by the equation $C_{55}H_{72}O_5N_4Mg + 2CO_2 + 2H_2O = C_{55}H_{74}O_5N_4 + Mg(HCO_3)_2$. Carbon dioxide has therefore the power of breaking the two links between the metal and nitrogen atoms in the molecule.

Before the magnesium is completely removed, however, an important intermediate compound, of the nature of a hydrogen carbonate, is formed. As this has the same colour as chlorophyll,

the subsidiary valency chromophoric complex is still existent, thus:



The evidence in favour of the existence of such an intermediate compound is as follows. (1) If a chlorophyll hydrosol is partly saturated with carbon dioxide, then extracted with ether, and the ash of the pigment is estimated, it will be found that the magnesium content is greater than it would be if the gas had directly eliminated the metal. (2) If partly saturated solutions are poured into alcohol (4 parts) and purified air is bubbled through the solution, all the carbon dioxide is recovered and chlorophyll is reproduced.

If the partly saturated hydrosols themselves are allowed to dissociate, however, the carbon dioxide is not quantitatively recovered. Hydrolysis takes place, which in the case of chlorophyll-*a* results in the quantitative formation of phæophytin and the basic carbonate, $4MgCO_3,Mg(OH)_2$. With chlorophyll-*b*, a certain amount of chlorophyll is regenerated.

The obvious suggestion is, therefore, that chlorophyll in the leaf unites with carbon dioxide in a similar way, but the conditions are not quite the same. The speed at which carbon dioxide is absorbed by the leaf is much greater than it is in the case of the hydrosol, and the leaf thrives in an atmosphere containing as much as 20% of carbon dioxide, which is a concentration that would very soon lead to the decomposition of chlorophyll in solution. At any rate, the photosynthesis which goes on in the leaf is now to be regarded as an action of the light on the compound of carbon dioxide and chlorophyll, which consists in transforming the carbonic acid into a peroxidic isomeride, capable of parting with oxygen in the gaseous form. Two isomerides are possible, namely, per-formic acid, H·CO·O·OH, which is known to change easily into carbonic acid (d'Ans and Frey, A., 1912, i, 601), and a hypothetical peroxide of formaldehyde, $OH{\cdot}CH{<}^{O}_{O}$. The latter possibility is discussed in the light of the fact that formaldehyde is the primary product in the photosynthesis of carbohydrates.

J. C. W.

The Permeability of Living Protoplasm to some Salts. ARTHUR TROENDLE (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 38—54, 117—132).—Salts in hypertonic solutions are absorbed at first with a constant velocity, characteristic for each salt, but after a certain quantity of the salt has been absorbed, the velocity of entry diminishes steadily. In the first stage there is a definite

ratio between the concentration and the time, and in the second stage there is a ratio between the concentration and the logarithm of the time. The entry of salts through living protoplasm does not obey Fick's law of diffusion. The nature of the cation controls the velocity of entry of a salt much more than that of the anion. In a group of chemical elements there is a concordance between the influence of an ion on the velocity of absorption and its position in the periodic classification of the elements. As an explanation of the experimental facts, the author suggests the following hypothesis. The salts irritate the protoplasm, which replies by transferring some of the salt to its interior. During this process, changes of an unknown character, designated by the term "fatigue," take place in the protoplasm. This fatigue, in increasing, obeys Weber's law. W. G.

Soluble Carbohydrates in Green Leaves. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1918, **101**, 77—88).—The author estimates the amounts of various soluble carbohydrates in the leaves of plants collected at a period when the products of assimilation are at a maximum. *Tulipa sylvestris* and *Narcissus poeticus* contain 1% of sucrose in the fresh leaf, together with dextrose and other soluble sugars, but no starch. There is no sucrose or starch in *Gentiana brevidens*, the place of the latter being taken by an apparently new saccharide which reduces Fehling's solution, possesses a lævorotation, and on hydrolysis yields only dextrose. It is present to the extent of 2·5%, calculated on the fresh leaves. *Hemerocallis fulva*, *Fritilaria imperialis*, *Allium victoriale*, and *Veratrum nigrum* contain from 2 to 3% of carbohydrates soluble in water, whilst *Scilla sibirica* and *Iris germanica* contain from 1—2%. There are only traces of starch and reducing sugars in *Convallaria majalis*, but a considerable quantity of a polysaccharide of the inulin type, yielding lævulose on hydrolysis with acetic acid. Of the plants in the leaves of which starch is present, *Hosta Sieboldiana* and *Tilia europæa*, containing moderate amounts of starch, also contain 1—2% of soluble carbohydrates, whereas in *Taraxacum officinale*, *Bunias orientalis*, and *Acer platanoides*, containing much starch, there are only traces of saccharides soluble in water. With the exception of *Convallaria*, the amount of starch in the leaves is roughly inversely proportional to the amount of soluble carbohydrates present. H. W. B.

Chemical Composition of "Assimilation-secretion" in Plants. ARTHUR MEYER (*Ber. Deut. bot. Ges.*, 1918, **35**, 674—680).—Previous investigations have shown that the globules (assimilation-secretion) occurring in chloroplasts may be differentiated from fat by microchemical means. They do not become crystalline on treatment with potassium hydroxide solution, and with strong nitric acid they exhibit pitting of the surface. They are soluble in alcohol, ether, or strong acetic acid, are turned brown by osmic acid, and reduce ammoniacal silver nitrate solution.

The total volume of the "secretion" in 1 kilo. of dark green

leaves of *Tropaeolum majus* is calculated to be approximately 0·5 c.c., and in old leaves of the same plant immediately prior to withering to be 2·14 c.c. The dried and powdered leaves of *Funkia Sieboldiana* on being heated at 120° gave a turbid distillate which possessed a characteristic odour and reduced ammoniacal silver nitrate solution.

The author assumes that the "assimilation-secretion" contains compounds related to the leaf-aldehyde isolated by Curtius and Franzen (compare A., 1912, ii, 797, 978, 979; 1914, i, 646), but it is also supposed that the "secretion" contains other constituents, since the amount of Δ^{a}-hexenaldehyde obtained by these investigators is much less than the total volume of the secretion observed by the author. H. B. H.

The Manganese Content of the Ash of certain Drugs. L. E. WESTMAN and R. M. ROWAT (*J. Amer. Chem. Soc.*, 1918, **40**, 558—562).—Manganese appears to be fairly widely distributed in the vegetable kingdom (compare Hafner and Krist, *Zeitsch. Oesterr. Apoth. Ver.*, 1907, **45**, 387; Pichard, A., 1899, ii, 40; Jadin and Astruc, A., 1913, i, 948; McHargue, A., 1915, i, 48; Headden, *J. Agric. Res.*, 1915, **5**, 349). The manganese content of certain laxative drugs and allied species of plants, for example, *Rhamnus frangula* (alder buckthorn bark), *Cinnamomum cassia cortex* (cassia bark), *Rhamnus purshiana* (cascara sagrada), podophyllin root, senna leaves, rhubarb root, *Rhamnus californica* bark, licorice root, jalap root, *Euonymus atropurpureus* (wahoo bark), cassia pulp, and Barbadoes aloes has been examined; the first two exhibit a higher content of manganese than any similar plant tissue hitherto examined; the figures are somewhat variable, the maximum being 0·067%. In *Rhamnus purshiana*, it is found that the proportion of manganese in the inner third of the bark is about twice as great as in the outer third. When the powdered drugs of the Rhamnaceæ family are extracted with water, approximately one-fourth of the manganese goes into solution. D. F. T.

The Degradation of Inulin and of the "Inulides" in Chicory Root. B. GESLIN and J. WOLFF (*Compt. rend.*, 1918, **166**, 428—430. Compare A., 1917, i, 720).—Chicory roots gathered in October or December and stored one month show a change in their inulin and inulide content. A portion of the inulin is converted into inulide, and some of the less readily fermented inulides undergo further degradation and are converted into the more readily fermented inulides. W. G.

Occurrence of Catechol and Quinol. EDMUND O. VON LIPPMANN (*Ber.*, 1918, **51**, 272).—During the long spell of dry weather at the end of the summer of 1917, the author found deposits of almost pure catechol on the inner surfaces of the bark cast early in the morning by some old plane trees, and quinol

adhering in dense rings to the viscous exudations at the wounds caused by grafting some pear-trees. J. C. W.

Microchemistry of Plants. VIII. Organic Crystalline Substances in Gentiana germanica. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1917, **35**, 653—657).—The occurrence of two distinct crystalline substances in the leaves of *Gentiana germanica* is recorded. The first of these is obtained as a sublimate of yellow, needle-like crystals when the dry leaves are subjected to microsublimation at moderate temperatures. This compound, to which the name *gentiolutein* is given, is insoluble in water, alcohol, glycerol, aqueous chloral hydrate, olive oil, or in 10% solutions of hydrochloric, sulphuric, or acetic acid, but is easily soluble in acetone. In barium and calcium hydroxide solutions, the crystals become deep brown and also give a transitory, bright bluish-green colour with calcium chloride solutions. Gentiolutein occurs not only in the leaves, but also in the stems and flowers of the above species, but could not be detected in *G. asclepiadea*, *G. ciliata*, or *G. pneumonanthe*, although *G. ciliata* yielded a colourless, crystalline substance, which, however, differed from gentiolutein in its relations to the various solvents. A second crystalline substance may be observed when, after removal of the epidermis, the leaf is immersed in distilled water, or when it is treated with 10% solutions of hydrochloric, sulphuric, or nitric acid, or with phenol, alcohol, or glycerol.

Evidence is adduced to show that neither of the substances observed is identical with gentiopicrin or gentianin; further chemical investigations are required. H. B. H.

Conversion of Quicklime in Soil. G. HAGER (*J. Landw.*, 1917, **65**, 245—311).—Evidence confirmatory of earlier observations is given to show that when an application of quicklime is made to the soil, only a small proportion of the lime reappears as calcium carbonate. The remainder is adsorbed by the soil constituents, and it is impossible to detect the presence of free calcium hydroxide after even a very short period of digestion. This adsorption of lime may be due to surface action or to chemical causes, and is regarded as being associated with the observed increased adsorptive power of a soil for other bases, such as potash and ammonia, which results from an application of lime.

The power of a soil for adsorption appears to be related to its content of clay and the presence of unsaturated compounds, and under normal conditions an equilibrium between the absorptive and adsorptive power of the soil carbon dioxide and the soil compounds respectively is soon reached. The action of calcium carbonate is stated to be less rapid than that of calcium oxide, and some months may elapse before an equilibrium is obtained. The influence of calcium oxide on the physical character of the soil is also discussed. H. B. H.

The Nitrogen Distribution of Fibrin Hydrolysed in the Presence of Ferric Chloride. CLARENCE AUSTIN MORROW and WALTER RAYMOND FETZER (*Soil Sci.*, 1918, **5**, 163—167).—With the view of obtaining more evidence on the formation of humin nitrogen in soils, fibrin was hydrolysed (1) alone, (2) in the presence of ten times its weight of anhydrous ferric chloride, and the resulting product was, in each case, analysed by the Van Slyke method. The results show that when a protein is hydrolysed in the presence of ferric chloride, an accurate nitrogen distribution cannot be obtained. There is a substantial increase in the ammonia nitrogen (from 10·48 to 13·17%), due to the presence of ferric chloride, owing probably to the higher temperature of hydrolysis, and consequent deamination of some amino-acids. The acid-soluble humin nitrogen increases (from 1·0 to 9·84%) at the expense of a corresponding loss in the filtrate from the bases. The earlier conclusion (compare A., 1917, i, 512) in regard to humin nitrogen precipitated by calcium hydroxide is therefore incorrect, a part of this acid-soluble humin being of protein origin instead of largely non-protein. Emphasis is laid on the fact that much of the recent work on the organic nitrogen distribution in soils by Van Slyke's method is entirely untrustworthy. [See also *Ind.*, May.]

W. G.

The Significance of the Sulphur in Ammonium Sulphate Applied to certain Soils. CHARLES B. LIPMAN and W. F. GERICKE (*Soil Sci.*, 1918, **5**, 81—86).—The superiority of ammonium sulphate as a nitrogenous fertiliser for barley (compare *ibid.*, 1916, **2**, 575) is apparently due to its sulphur content, the sulphur combined with the nitrogen producing the effect. [See, further, *Ind.*, 252A.]

W. G.

Some Availability Studies with Ammonium Phosphate and its Chemical and Biological Effects on the Soil. F. E. ALLISON (*Soil Sci.*, 1918, **5**, 1—80).—A comparison of commercial ammonium phosphate with ammonium sulphate, organic fertilisers, and certain phosphatic fertilisers. Ammonium phosphate nitrifies at approximately the same rate as ammonium sulphate, whilst organic nitrogenous manures, such as dried blood and cottonseed meal, are much less available. Calcium carbonate proved favourable to nitrification, but calcium oxide sometimes caused a depression in the nitrification of the two ammonium salts. There was apparently but little difference in the availability of the phosphorus in ammonium phosphate, acid phosphate, and basic slag, but raw rock phosphate was much less available.

For details of manufacture of the ammonium phosphate and comparative cropping tests with the various fertilisers, see *Ind.*, 252A.

W. G.

Organic Chemistry.

Revision of the Tables for the Strength of Ethyl Alcohol. N. Schoorl and (Miss) A. Regenbogen (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 831—837, and *Pharm. Weekblad*, 1918, **55**, 390—409).—In view of the preparation of a new edition of the Dutch Pharmacopœia, measurements have been made of the density of mixtures of ethyl alcohol and water at 15°. The results obtained are in agreement with those obtained by Osborne and MacKelvy (compare A., 1912, i, 232), and the authors recommend the table of the Bureau of Standards (Washington) as affording the most accurate values of the densities of alcohol–water mixtures. [See also *J. Soc. Chem. Ind.*, 318A.] H. M. D.

Preparation of Amylene Bromohydrin (Bromoamyl Alcohol). Emil Rath (D.R.-P., 301905; from *Chem. Zentr.*, 1918, i, 53).—Mixtures of hypobromites and such acids as boric acid yield with amylene (β-methyl-Δ^{β}-butylene) in the cold the bromohydrin, which may be useful in the production of pharmaceutical preparations. J. C. W.

New Molybdyl Compound. Ricardo Montequi Díaz de Plaza (*Anal. Fis. Quim.*, 1910, **14**, 542—548; from *Chem. Abstr.*, 1917, **11**, 2864—2865).—When aqueous solutions of ammonium molybdate and potassium *iso*butylxanthate are mixed, the liquid after a time assumes a dark violet colour, and when acidified by the gradual addition of acetic acid, a dark-coloured substance, consisting of a mixture of $(C_5H_9OS_2)_4,Mo_2O_3$ and $(C_5H_9OS_2)_2$, is precipitated. When the precipitate is dried and extracted with light petroleum, the latter substance is removed.

The molybdenum compound forms nearly black, monoclinic crystals, m. p. 105°, insoluble in water, slightly soluble with purple colour in cold, and with greenish-blue colour in hot, ethyl alcohol, and readily soluble in acetone, benzene, toluene, carbon disulphide, chloroform, or ethyl ether with intense purple coloration. It is not acted on in the cold by concentrated hydrochloric or sulphuric acid. It is oxidised by nitric acid, and dissolves readily in potassium hydroxide solution, but not in ammonia. H. M. D.

Configuration of Organic Compounds and their Relation to Chemical and Physical Properties. Arthur Michael (*J. Amer. Chem. Soc.*, 1918, **40**, 704—723).—A theoretical paper in which the author discusses the relationships between the free and bound energy, and entropy changes with the spacial arrangement of the atoms in stereoisomerides. The influence of olefinoid unsaturation and configuration on the affinity constants of acids is discussed in the cases of aliphatic acids, dibasic unsaturated acids, and the cinnamic acids. T. H. P.

Relative Stabilities of Halogen-substituted Aliphatic Acids in Aqueous Solution. II. The Propionic and Butyric Acid Series. G. S. SIMPSON (*J. Amer. Chem. Soc.*, 1918, **40**, 674—683. Compare this vol., i, 57).—The hydroxylation of halogen derivatives of propionic and butyric acids has been studied by keeping 0·1*N*-solutions of their sodium salts at 70° and titrating the sodium haloid formed at different intervals. The following order of stability is established:—*propionic* acid series: β-bromo-, β-iodo-, α-bromo-, β-chloro-, αα-dibromo-, αβ-dibromo-, α-chloro-, αβ-dichloro-, of the order 1, 1·03, 3·31, 7·17, 10·96, 18·68, 37·06, 186·8; *butyric* acid series: α-bromo*iso*-, β-chloro-, α-bromo-, α-chloro-, of the order 1, 277, 374, 6171.

From these figures, the following points are apparent: (1) chlorine-substituted acids are more stable than analogous bromine or iodine compounds; (2) iodine compounds are sometimes more stable than bromine analogues; (3) α-halogen acids are more stable than their β-isomerides, and position is of greater moment than the nature of the halogeu; (4) if the hydrogen atoms in the $-CH_2Hal.$ or $-CHHal.-$ groups are replaced by alkyl radicles, the stability of the acids is diminished, and the larger the alkyl group, the greater is the weakening effect; (5) a second halogen atom in the α-position renders the removal of a halogen in the α- or β-position more difficult.

Some brief notes on the preparation of the various acids are given, and the bearing of some of the results on problems connected with the hydrolysis of the salts (compare Senter and others) is discussed. J. C. W.

Synthesis and Oxidation of Tertiary Hydrocarbons. P. A. LEVENE and L. H. CRETCHER, jun. (*J. Biol. Chem.*, 1918, **33**, 505—512).—The tertiary hydrocarbons are prepared by the reduction of acids obtained by the malonic ester synthesis.

Ethyl dibutylmalonate, $C(C_4H_9)_2(CO_2Et)_2$, is formed by the action of butyl iodide and sodium ethoxide on ethyl malonate. The introduction of the first butyl radicle must be completed before that of the second is attempted. The attempt to effect both substitutions at the same time by heating the malonic ester with two molecules of the ethoxide and iodide gives unsatisfactory results. Ethyl dibutylmalonate hoils at 153—154°/14 mm. (corr.). On saponification, *dibutylmalonic acid*, $C_{11}H_{20}O_4$, is obtained. It crystallises from benzene in long, prismatic needles, m. p. 163° (decomp.). On heating at 180°, carbon dioxide is evolved, and at 255° (corr.), *α-butylhexoic acid*, $CH(C_4H_9)_2{\cdot}CO_2H$, distils over; this has b. p. 153°/16 mm. and D^{16} 0·899. The ester, *ethyl α-butylhexoate*, $C_{12}H_{24}O_2$, is prepared by boiling the acid with alcohol and a little sulphuric acid for eight hours, and has b. p. 114—115°/15 mm. (corr.). The reduction of the ester to the corresponding alcohol is accomplished by Levene and Allen's method (A., 1917, i, 3), the yield being 65 to 70% of that theoretically possible. *β-Butylhexyl alcohol*, $C_{10}H_{22}O$, has b. p. 218—219°

(corr.) and D 0·836. On boiling the alcohol with three molecules of hydriodic acid for five hours, an 80% yield of *β-butylhexyl iodide*, $C_{10}H_{21}I$, is obtained, b. p. 124—125°/13 mm., D 1·267, and reduction of the iodide with zinc and glacial acetic acid yields *β-butylhexane*, $C_{10}H_{22}$, b. p. 165° (corr.), D 0·738.

When β-butylhexyl iodide is slowly added to an excess of the monosodium derivative of ethyl malonate in alcohol and the mixture boiled, *ethyl β-butylhexylmalonate*, $C_{17}H_{32}O_4$, b. p. 180°/14 mm., is produced, which on saponification yields *β-butylhexylmalonic acid*, $C_{13}H_{24}O_4$, rhombic needles from light petroleum, m. p. 88° (corr.). The following compounds are prepared by the methods already indicated in the case of the β-butylhexane derivatives: *γ-butyloctoic acid*, $C_{12}H_{24}O_2$, b. p. 173—174°/12 mm. (corr.), D 0·901; *ethyl γ-butyloctoate*, $C_{14}H_{28}O_2$, b. p. 139°/10 mm. (corr.); *δ-butyloctyl alcohol*, $C_{12}H_{26}O$, b. p. 139°/15 mm., D 0·841; and *δ-butyloctyl iodide*, $C_{12}H_{25}I$, b. p. 143°/8 mm., D 1·194.

β-Butylhexane is readily oxidised at 80—90° by an alkaline solution of permanganate, but the only oxidation products which can be detected are formic acid and carbon dioxide. At 25°, a small amount of butyric acid is formed, which is recognised by its silver salt. H. W. B.

Preparation of Acetaldehyde. H. Dreyfus (Brit. Pat. 105064).—Acetylene which has been freed from such impurities as hydrogen sulphide, hydrogen phosphide, and ammonia, is passed, under a pressure of about 1·5 atm., into a solution containing 10—15% of sulphuric acid and from 1 to 10%, preferably 3—6%, of mercury. The liquid is kept at 25—40°, and the gas is passed in slowly, with vigorous agitation, until the precipitated mercury compound becomes grey or greyish-black, and then as rapidly as the liquid will absorb it. At intervals, the temperature is raised to not above 50—60° to distil off the acetaldehyde. A yield of acetaldehyde equivalent to 90—95% of the quantity of acetylene, or five to ten times that of the mercury compound used, is obtained. [See, further, *J. Soc. Chem. Ind.*, 1918, 222A.] A. S.

The Crotonisation of Acetaldehyde. Formation of Butanol and Hexanol from Ethyl Alcohol. Paul Sabatier and Georges Gaudion (*Compt. rend.*, 1918, **166**, 632—636).—Acetaldehyde when passed over the oxides of thorium, titanium, or uranium at 360° undergoes crotonisation and gives crotonaldehyde, hexadienaldehyde, and a certain amount of higher homologues. If ethyl alcohol is used as the starting material, it is passed first over reduced copper at 300°, and the resulting vapours are then passed over uranium oxide at 360°, or the vapours of the alcohol may be passed slowly over uranium oxide at 360°, when they undergo dehydrogenation and dehydration in the one process. The best yield of crotonaldehyde is obtained by vaporising paracetaldehyde and passing these vapours over the catalyst. If the products of the crotonisation are roughly fractionally distilled and the fractions boiling at about 90—130° and 130—220° passed

with hydrogen over reduced nickel at 170—180°, normal butyl alcohol and normal hexanol are obtained. W. G.

Acetone and Lime. M. E. Freudenheim (*J. Physical Chem.*, 1918, **22**, 184—193).—When acetone vapour is passed over slaked lime in a tube heated at temperatures varying from 350° to 630°, calcium carbonate and carbon are left in the tube, the amount of carbon being small at low temperatures, but rapidly increasing with a rise in temperature. The gas evolved consists of methane, hydrogen, carbon monoxide, ethylene, and carbon dioxide. The amount of gas decreases during the run, and the percentage of hydrogen also shows a tendency to decrease, whilst the percentage of methane increases; the percentages of carbon monoxide and olefines remain practically constant at 16% and 4% respectively. At 350°, the gaseous products are nearly 80% hydrogen and 20% methane; at 650° methane is the chief gaseous product.

It is thought that acetone may be an intermediate product of the action of lime on calcium acetate, and that its dissociation may account for the presence of carbon monoxide, thus: $CH_3\cdot CO\cdot CH_3 = CH_4 + CO + C + H_2$, whilst the ethylene may owe its formation to the production of methane and keten, the latter breaking down into carbon monoxide and ethylene, thus: $CH_3\cdot CO\cdot CH_3 = CH_4 + CH_2\colon CO$, $2CH_2\colon CO = 2CO + C_2H_4$. The production of hydrogen and methane only at 350° cannot be accounted for satisfactorily, though it is known that hydrogen is also set free when sodium acetate is heated with soda lime.

When acetone is passed over heated nickel, carbon is precipitated and some of the excess of acetone is reduced to *iso*propyl alcohol, and it is stated that the decreasing percentage of hydrogen evolved at higher temperatures is probably due to its action on the acetone, with formation of *iso*propyl alcohol. [See also *J. Soc. Chem. Ind.*, 282A.] B. N.

Synthesis of Two Isomeric Series of Alkylthioglucosides. Wilhelm Schneider, Johanna Sepp, and Ottilie Stiehler (*Ber.*, 1918, **51**, 220—234. Compare A., 1916, i, 792).—The reaction by which glucose mercaptals may be converted into alkylthioglucosides, namely, by treatment with one molecular proportion of mercuric chloride, has been extended from the ethyl to the methyl, *n*-propyl, and benzyl compounds. The products obtained in this way happen to be all α-glucosides, but the isomeric β-glucosides can also be formed, the mode of preparation depending on the interaction of the potassium salts of mercaptans with acetobromoglucose. Compared with the α- and β-methylglucosides, the two series of thioglucosides show a remarkable difference; the β-isomerides are much more stable towards dilute mineral acids than the α-compounds in this case. The thioglucosides are also non-acidic, whereas the mercaptals dissolve in alkali hydroxides.

The new mercaptals were again prepared by Fischer's method, namely, condensation of glucose with the thiol under the influence

of concentrated hydrochloric acid. *Glucose methyl mercaptal*, $C_6H_{12}O_5(SMe)_2$, has m. p. 161°, $[\alpha]_D^{24}$ in *N*-sodium hydroxide, −20·76°, and forms a *penta-acetate*, m. p. 83°, $[\alpha]_D^{20}$ in *s*-tetrachloroethane, +38·71°; *a-methylthioglucoside*, $C_6H_{11}O_5 \cdot SMe$, crystallises in slender needles, m. p. 137°, $[\alpha]_D^{20}$ in water, +124·5°, and its *tetra-acetate* has m. p. 89°, $[\alpha]_D^{22}$ in *s*-tetrachloroethane, +150·0. *Penta-acetylglucose ethyl mercaptal*, m. p. 42—45°, $[\alpha]_D^{20}$ +17·71°, is very stable towards mercuric chloride, and cannot be converted by its agency into the tetra-acetyl derivative of true, aldehydic glucose. *Glucose* n-*propyl mercaptal* forms slender leaflets, m. p. 146°, and *a*-n-*propylthioglucoside* has m. p. 118—122°, $[\alpha]_D^{24}$ in water, +116·5°. *a-Benzylthioglucoside* has m. p. 112—114° (viscous), 118° (mobile), $[\alpha]_D^{25}$ +175·7°, and forms a *tetra-acetate*, prismatic needles, m. p. 77°, $[\alpha]_D^{23}$ +186·3°; *penta-acetylglucose benzyl mercaptal* has m. p. 64°, $[\alpha]_D^{20}$ +31·75°.

The hydrolysis of *a*-ethylthioglucoside has been examined. It is unaffected by maltase, emulsin, or myrosin; with 1% hydrochloric acid at 25°, equilibrium is reached in thirty-four hours, when 94—95% has been hydrolysed, but with 2·5% hydrochloric acid, the same result is obtained in eight to nine hours.

Acetobromoglucose and potassium methyl sulphide react in methyl-alcoholic solution to form *tetra-acetyl-β-methylthioglucoside*, slender needles, m. p. 93°, $[\alpha]_D^{20}$ in *s*-tetrachloroethane, −14·67°, which is hydrolysed by barium hydroxide solution in the cold to *β-methylthioglucoside*, a syrup with $[\alpha]_D^{15}$ −18·14°. Partial hydrolysis takes place in the first stage, so the crude product is heated with acetic anhydride and sodium acetate before purification. *Tetra-acetyl-β-ethylthioglucoside* crystallises in needles, m. p. 78—79°, $[\alpha]_D^{26}$ −22·27°, and forms a compound, m. p. 83—84°, with ordinary tetra-acetyl-*β*-ethylglucoside; *β-ethylthioglucoside* forms stout, rectangular prisms, $1H_2O$, m. p. 46—47°, the anhydrous substance having m. p. 99—100°, $[\alpha]_D^{21}$ −55·14°. *Tetra-acetyl-β-benzylthioglucoside* has m. p. 98°, $[\alpha]_D^{24}$ −93·1°, and *β-benzylthioglucoside* is a syrup.

β-Ethylthioglucoside is unaffected by emulsin, myrosin, or maltase, and is not perceptibly altered by hydrochloric acid unless the concentration is at least 5% and the temperature 70—80°.

J. C. W.

Structure of Crystalline β-Methylfructoside. Ettie Stewart Steele (T., 1918, **113**, 257—263).—Recent investigations (Irvine and Robertson, A., 1917, i, 79) have shown that it is very probable that the syrup obtained by condensing fructose with methyl alcohol contains the *a*- and *β*-modifications of both butylene-oxidic and ethylene-oxidic methylfructosides. The mixture may be methylated by means of silver oxide and methyl iodide, and the product converted by hydrolysis into a mixture of tetramethylfructoses, consisting of a crystalline and a syrupy variety (Purdie and Paul, T., 1907, **91**, 289). The same crystalline tetramethylfructose has now been obtained by similar treatment of Hudson's

crystalline β-methylfructoside (A., 1916, i, 547), which is stable towards permanganate, that is, conforms to the butylene oxide type. The crystalline tetramethylfructose must therefore be butylene-oxidic, or, in other words, the original mixture of β-methylfructosides contains Hudson's γ-oxidic isomeride.

The action of acetic anhydride on fructose, in the presence of zinc chloride, yields about equal quantities of crystalline and syrupy products. The solid portion is stable towards permanganate, and is the tetra-acetate from which Hudson prepared his *β-methylfructoside*. *It may be acetylated completely, and is* derived, therefore, from butylene-oxidic fructose. The syrup is apparently a triacetate, which resists further acetylation, may be converted into a mono-methyl ether (not a methylfructoside triacetate), and very readily reduces permanganate. It is therefore derived from ethylene-oxidic fructose. J. C. W.

Preparation of a Salt of Fructosediphosphoric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 302094; from *Chem. Zentr.*, 1918, i, 249).—The calcium salt of fructosediphosphoric acid (from metaphosphoric esters and fructose) is only sparingly soluble, but is, nevertheless, easily absorbed in the *organism, and is claimed to be good in such cases as rickets.*

J. C. W.

The Digestibility of Bread. III. Erythrodextrin in Starch Hydrolysis. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1918, **40**, 623—636. Compare A., 1916, i, 578; 1917, i, 361).—In the previous communication, it was shown that the digestion of erythrodextrin is a unimolecular reaction. It might therefore be used in order to determine amylolytic activity, and, consequently, efforts have been made to obtain pure erythrodextrin for such purposes. In this connexion, the present paper describes some new studies on the degradation of starch by (*a*) heating starch moistened with 0·1*N*-hydrochloric acid at 85°, and (*b*) boiling starch with about 0·032*N*-hydrochloric acid, and also new methods for estimating the products by measuring the colorations produced by iodine water. It is expected that it will soon be possible to prepare pure erythrodextrin.

It appears that the cleavage of boiled starch takes place in at *least three stages, protein and amylodextrin preceding* erythramylum (rose-amylose) and erythrodextrin in order of formation. These stages probably correspond with the stages of salivary digestion and the degradation by roasting.

A number of supplementary notes are recorded. (1) "Artificial starch," the substance which crystallises at about 50° on cooling a partly hydrolysed solution of starch, is a solid solution of amylodextrin and erythrodextrin in higher polysaccharides. (2) Lintner's "soluble starch" is almost pure amylodextrin, crystallising with difficulty only at temperatures below 50°, and forming an iodide, the transition temperature of which, in 1% solutions, is 69·5°. (3) Amylodextrin appears to be an individual substance, fairly

soluble in cold water, but not in 40% alcohol; it gives a blue iodide which has the maximum transition point, 74°; it probably yields erythrodextrin on hydrolysis. (4) Erythrodextrin is insoluble in 49—67% alcohol; the transition point of its iodide is 64°; it yields achroodextrin on hydrolysis, but in the "roasting" process it appears to be the final polysaccharide. (5) Erythramylum is formed simultaneously with erythrodextrin, and probably changes into amylodextrin on hydrolysis; it is precipitated by 35% alcohol.

J. C. W.

Preparation of Taurine in Large Quantities. CARL L. A. SCHMIDT and THOMAS WATSON (*J. Biol. Chem.*, 1918, **33**, 499—500).—Taurine is readily prepared from the abalone, *Haliotis*, which can be obtained in quantity on the Pacific coast. The shell and intestinal tract are removed, and the muscle is then finely minced and the juice pressed out. Protein is removed from the juice by precipitation with acetic acid, and the filtrate hydrolysed with hydrochloric acid. After concentration, the taurine is precipitated by alcohol, and finally recrystallised from water. Eight dozen abalones (74 kilograms of muscle) yield 362 grams of taurine.

H. W. B.

Interaction of Formaldehyde and Carbamide. AUGUSTUS EDWARD DIXON (T., 1918, **113**, 238—248).—A number of experiments on the condensation of carbamide with formaldehyde (37·5% solution) are described. Equimolecular proportions, just neutralised with dilute sodium hydroxide, yield on evaporation in a desiccator methylolcarbamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot OH$, which gives no reaction for formaldehyde unless acidified. With a double proportion of formaldehyde, under the same conditions, the product is dimethylolcarbamide, $CO(NH\cdot CH_2\cdot OH)_2$, which changes at about 123° or when treated with dilute hydrochloric acid into the compound, $CO<\begin{matrix}NH\text{------}CH_2\cdot NH\\N(CH_2\cdot OH)\cdot CH_2\cdot NH\end{matrix}>CO$, thus, $2C_3H_8O_3N_2 \rightarrow C_5H_{10}O_3N_4 + CH_2O + 2H_2O$. The two methylol derivatives have already been described by Einhorn and Hamburger (A., 1908, i, 141), and the third product is Goldschmidt's compound (A., 1897, i, 22; 1898, i, 178).

When condensation between formaldehyde and carbamide is catalysed by small quantities of acids, granular precipitates usually appear very quickly. They vary in composition, but display as a common feature black crosses in plane polarised light. With 0·75 mol. of formaldehyde, the product is dimeric methylene carbamide, presumably formed, in the presence of small quantities of acids, from the initial methylolcarbamide, thus:

$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot OH \rightarrow NH_2\cdot CO\cdot NH\cdot CH_2X \rightarrow$$

$$HX + \cdot NH\cdot CO\cdot NH\cdot CH_2\cdot \rightarrow CO<\begin{matrix}NH\cdot CH_2\cdot NH\\NH\cdot CH_2\cdot NH\end{matrix}>CO$$

With 1·5 to more than 2 mols., the sole product is Goldschmidt's compound, probably formed by the action of formaldehyde on

"nascent" monomeric methylenecarbamide. With 4 mols., the precipitate is scanty and consists of a substance probably of the formula $CH_2(NH·CO·NH·CH_2·OH)_2$, whilst with 11 mols. condensation ceases. J. C. W.

Thiocyanates and Thiocarbimides. XII. The Polyketide Thiocarbimide, Ethyl α-Thiocarbiminopropionate. TREAT B. JOHNSON and ARTHUR A. TICKNOR (*J. Amer. Chem. Soc.*, 1900, **40**, 636—646. Compare A., 1916, i, 635, 717).—Inactive ethyl α-thiocyanopropionate (I) was prepared by Wheeler and Barnes from the α-bromopropionate and potassium thiocyanate (A., 1900, i, 566). The inactive and dextrorotatory forms of the isomeric ethyl α-thiocarbiminopropionate (II) have now been obtained by the interaction of thiocarbonyl chloride and the ethyl α-aminopropionates.

$N⋮C·S·CHMe·CO_2Et$ (I.) $S⋮C⋮N·CHMe·CO_2Et$ (II.)

Racemic alanine hydrochloride is most conveniently prepared by conducting the crude acetaldehyde from the oxidation of alcohol directly into a solution of commercial sodium cyanide, ammonium chloride, and ammonia, and after twenty-four hours acidifying and evaporating to dryness. The free ester (3 mols.) reacts vigorously with thiocarbonyl chloride (1 mol.) in dry ether, and the hydrochloride reacts with rather more than one molecular proportion of thiocarbonyl chloride in boiling toluene, giving the *hydrochloride* of *ethyl* dl-*α-thiocarbiminopropionate*, m. p. 87°. The free *ester*, obtained on distillation of the salt, is a pale yellow oil, b. p. 93·5—94·5°/13 mm., D 1·0994 (average), n_D^{20} 1·4915. Similarly, active alanine ester hydrochloride gives rise to *ethyl* d-*α-thiocarbiminopropionate*, b. p. 100—101°/11—12 mm., n_D^{20} 1·4935, $[\alpha]_D^{20}$ +29·77°, but the free amino-acid does not react in this way.

As a thiocarbimide, the inactive ester reacts with aniline to form *ethyl phenyl-α-methylthiohydantoate*,

$NHPh·CS·NH·CHMe·CO_2Et$,

which crystallises in rosettes, m. p. 83—84°. Inactive ethyl alanine and phenylthiocarbimide apparently produce the same compound, but the reaction is so vigorous that this loses alcohol, and so the actual product is *2-thio-1-phenyl-4-methylhydantoin*, $CS<\begin{matrix}NPh·CO\\NH-CHMe\end{matrix}$, m. p. 183·5—184·5° (compare Aschan, A., 1883, 1107).

Furthermore, the ester reacts with hot alcohol to form the *thionurethane*, $OEt·CS·NH·CHMe·CO_2Et$, in slender prisms, m. p. 55·5—56°, b. p. 157—159°/18 mm. J. C. W.

New Preparation of Nitriles by Catalysis of Primary Amines. ALPH. MAILHE and F. DE GODON (*J. Pharm. Chim.*, 1917, [vii], **16**, 225—229).—A claim for priority over Sabatier and

Gaudion (compare A., 1917, ii, 460) for the use of reduced copper or reduced nickel as catalysts for the conversion of primary amines into the corresponding nitriles. The present authors had deposited the details of their process in a sealed communication in March, 1917. W. G.

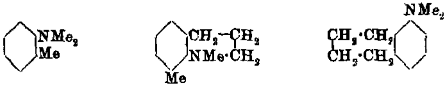
Preparation of Halogenated Arsinic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 296915; from *Chem. Zentr.*, 1917, i, 715).—Hydrocarbons of the acetylene series are treated with arsenic trihaloids, or mixtures which yield these compounds, and the products are converted into arsenoxides and then into arsinic acids by oxidation. Thus, heptinene gives "heptinenechloroarsenoxide," a dark syrup, and "*heptinenechloroarsinic acid*" [?, *β-chloro-Δ^α-heptenylarsinic acid*, $C_5H_{11}\cdot CCl:CH\cdot AsO(OH)_2$], white needles, m. p. 115°, the sodium salt of which is freely soluble in water. Octinene yields "octinenebromoarsenoxide" and "octinenebromoarsinic acid" [?, *β-bromo-Δ^α-octenylarsinic acid*], m. p. 129—130°. J. C. W.

Werner's Theory of Valency and Benzene. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 400—405).—The author is of opinion that Werner's theory of valency is not adapted to account for the structure and properties of benzene and its derivatives. A. J. W.

Sulphite Turpentine. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1918, **10**, 258—260).—The so-called sulphite turpentine, obtained as a by-product in the manufacture of wood pulp by the sulphite process, consists in the main of cymene, and may be utilised in the production of toluene and carvacrol. Cymene-2-sulphonic acid forms a characteristic barium salt, $(C_{10}H_{13}SO_3)_2Ba,3H_2O$, which is sparingly soluble in water and crystallises in lustrous plates. On heating the anhydrous barium salt of the 2-sulphonic acid with an equal weight of phosphorus pentachloride, and forming the amide by heating with ammonia, a yield of 70·7 per cent. of the theoretical amount of cymenesulphonamide, m. p. 114°, was obtained. By oxidation with potassium permanganate, the cymene was converted into *p*-hydroxy*iso*propylbenzoic acid, m. p. 155°. Cymene also reacts readily with chlorosulphonic acid, and the resulting product may be converted into the sulphonamide by heating it with strong ammonia solution on the boiling water-bath. This reaction affords a convenient method of identifying pure cymene. When the sodium salt of cymene-2-sulphonic acid is fused with alkali at about 300°, carvacrol is produced in small quantity, and may be purified by converting it into carvacrol nitrite, m. p. 150—152°, which is insoluble in light petroleum. [See also *J. Soc. Chem. Ind.*, 296A.] C. A. M.

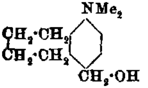
Steric Hindrance. IV. J. VON BRAUN, Z. ARKUSZEWSKI, and Z. KÖHLER (*Ber.*, 1918, **51**, 282—296).—Comparing dimethyl-*o*-

toluidine (I) with 1:8-dimethyltetrahydroquinoline (II), von Braun was surprised to find that the retarding influence of the *o*-methyl group on the reactivity of the nitrogen atom and the carbon atom opposite to it is considerably less in II than in I (A., 1916, i, 647). It is now found that when the methyl group is extended to a ring, as in III, its influence is also very much less.

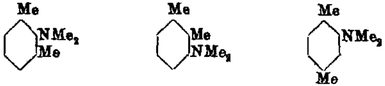


(I.) (II.) (III.)

5 : 6 : 7 : 8-Tetrahydro-α-naphthyldimethylamine (III) (Bamberger and Helwig, A., 1889, 891) reacts with methyl iodide more readily than dimethyl-*o*-toluidine, and when warmed with cyanogen bromide yields the *tetrahydro-α-naphthylcyanomethylamine*, b. p. 179—180°/7 mm., which may be hydrolysed by boiling with 25% hydrochloric acid to 5:6:7:8-*tetrahydro-α-naphthylmethylamine*, a pale yellow oil, b. p. 150—152°/12 mm. (*picrate*, m. p. 174°; *thiocarbamide* derivative, m. p. 113°). The base also reacts with formaldehyde, giving, after twenty-four hours' warming with formalin and concentrated hydrochloric acid, 4-*hydroxymethyl*-5 : 6 : 7 : 8-*tetrahydro-α-naphthyldimethylamine* (annexed formula), as a very viscous, yellow oil, b. p. 189—196°/10 mm. (*picrate*, m. p. 92—94°). Further reactivities of the para-carbon atom are exhibited by the formation of a nitroso-compound (*ibid.*) and by coupling with diazotised sulphanilic acid.



This weakening of the influence of the *o*-methyl group is not due to ring formation, as was previously supposed, for whilst dimethyl-2-*m*-xylidine (IV) is even less reactive than dimethyl-*o*-toluidine, dimethyl-2-*p*-xylidine (VI) is more reactive, and dimethyl-3-*o*-xylidine (V) is more reactive still.



(IV.) (V.) (VI.)

Thus, dimethyl-3-*o*-xylidine forms about three times as much methiodide in a given time as dimethyl-*o*-toluidine; when warmed with zinc chloride and benzaldehyde for five minutes and then mixed with chloroanil, it gives a distinct malachite-green colour, and when heated with "formalin" and concentrated hydrochloric acid, it yields 4-*dimethylamino*-2:3-*dimethylbenzyl alcohol*,

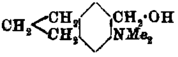
$$NMe_2{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}OH,$$

b. p. 149—152°/5 mm. (*picrate*, m. p. 112°; *platinichloride*, m. p. 192°; *methiodide*, m. p. 176°).

Similarly, *dimethyl*-2-p-*xylidine* (VI), b. p. 204° (*picrate*, m. p. 158°; *platinichloride*, m. p. 196°) reacts almost as sluggishly as dimethyl-*o*-toluidine with methyl iodide, forming the *methiodide*, m. p. 202°, but yields *4-dimethylamino*-2:5-*dimethylbenzyl alcohol* when condensed with formaldehyde, this being a pale yellow, very viscous oil, b. p. 168—170°/20 mm., which gives a *picrate*, m. p. 114°, a *methiodide*, m. p. 180°, and a *platinichloride*, m. p. 188°.

The conclusion is therefore drawn that the nitrogen atom and para-carbon atom are so inert in dimethyl-*o*-toluidine because the *o*-methyl group and the nitrogen atom are linked by residual affinity. This link is weakened if a meta-substituent is introduced, as the ortho- and meta-groups will then be similarly united, and the nitrogen atom will be more free to react. There is not so much likelihood of a union between a para-substituent and the nitrogen atom, and therefore a meta-group should not have much influence on the activities of a para-substituted tertiary amine. This point has been tested in the case of the base (annexed formula), which actually resembles dimethyl-*p*-toluidine in reactions.

The base is synthesised as follows: technical indene is hydrogenated in the presence of palladous chloride, the hydrindene is nitrated at −5°, the mixture of much *m*- with little *o*-nitrohydrindene is reduced with iron powder and acetic acid, and the mixture of primary amines is warmed with methyl iodide and sodium carbonate. A small quantity of *o-dimethylaminohydrindene*, b. p. 130—131°/20 mm. (*picrate*, m. p. 147°; *platinichloride*, m. p. 185—186°; *methiodide*, m. p. 202°), is formed, but the main product is the *quaternary iodide*, leaflets, m. p. 190°, of the desired m-*dimethylaminohydrindene* (above). This is obtained by distilling the methiodide, as an oil, b. p. 136—138°/18 mm., which forms a *picrate*, m. p. 160—161°, a *platinichloride*, m. p. 170—175°, a red *nitro*-compound, m. p. 85—86°, and a *thiocarbamide* derivative, m. p. 118°, and reacts with formaldehyde and concentrated hydrochloric acid to yield 5-*dimethylamino*-6-*hydroxymethylhydrindene* (annexed formula).



The latter is a very viscous, pale yellow liquid, b. p. 200°/31 mm., which gives a *picrate*, m. p. 144°, a *platinichloride*, m. p. 178° (decomp.), and a *methiodide*, m. p. 177°.

J. C. W.

Preparation of Tertiary Amines. OSKAR MATTER (D.-R.P., 301450 and 301832; from *Chem. Zentr.*, 1918, i, 53, 149).—Chlorine derivatives of the hydrocarbons are heated with sodamide, the mixture being stirred, and, if necessary, agents like copper gauze or copper powder being employed as catalysts. Thus, chlorobenzene yields triphenylamine, benzyl chloride at 110—120° gives

tribenzylamine, and *iso*amyl chloride at 210—220° forms tri*iso*-amylamine.

Mixtures of the chlorine compound and a primary amine may also be heated with sodamide, when, if the amine contains a different radicle, a mixed *tert.-amine* results. Thus, benzyl chloride, benzylamine, and sodamide, at 100—110°, yield tribenzylamine, benzyl chloride and aniline produce dibenzylaniline, and benzyl chloride and *p*-toluidine give dibenzyl-*p*-toluidine.

J. C. W.

Preparation of a Sparingly Soluble Complex Compound from Dimethylaniline, Benzyl Chloride, and Zinc Chloride. CHEMICAL WORKS, ROHNER & Co. (Brit. Pat. 104676).—A mixture of one molecular proportion of benzyl chloride and of dimethylaniline respectively is stirred with an aqueous solution of rather *more than half a molecular proportion of zinc chloride* until the separation of crystals of phenylbenzyldimethylammonium zincichloride is complete.

A. S.

Separation of Cresols. G. A. DARZENS (Brit. Pat. 107961).—*p*-Cresol and *m*-cresol are separated from mixtures by converting them into additive products with oxalic acid and with anhydrous sodium acetate respectively in the presence of a suitable solvent and with exclusion of moisture. The additive product is separated by filtration and subsequently decomposed by water. If *o*-cresol is also present, it is separated by a preliminary fractional distillation in a vacuum. [See, further, *J. Soc. Chem. Ind.*, 1918, 235A.]

A. S.

Preparation of Carbamic Esters and their *N*-Alkyl Derivatives, and Carbonic Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 296889; from *Chem. Zentr.*, 1917, i, 714).—Homologues of phenol, except the cresols, are converted into carbonates or carbamates in the usual way. The products are odourless and tasteless, and have anthelmintic properties. Thus, *p-tert.*-butylphenol reacts with carbonyl chloride to form p-tert.-*butylphenyl carbonate*, $CO(O\cdot C_6H_4\cdot CMe_3)_2$, m. p. 108°, in the presence of pyridine, and p-tert.-*butylphenyl* N-*dimethylcarbamate*, $NMe_2\cdot CO_2\cdot C_6H_4\cdot CMe_3$, m. p. 92°, in the presence of dimethylamine, whilst the corresponding *carbamate* crystallises in platelets or needles, m. p. 123—124°. p-iso*Amylphenyl carbamate* has m. p. 73—74°, p-*benzylphenyl carbamate*, m. p. 144°, p-iso-*propylphenyl carbamate*, m. p. 93—95°, and o-*allylphenyl carbamate*, m. p. 122—123°.

J. C. W.

[*p*-Benzylphenyl Carbamate.] SYNTHETIC PATENTS Co. (U.S. Pat. 1252452).—The carbonyl derivatives of phenols, of the general formula $R\cdot C_6H_4\cdot O\cdot CO\cdot R'$, in which R is a substituent with more than *one carbon atom* and R′ is $O\cdot C_6H_4R$ or NXX', X and X′ being respectively either a hydrogen atom or an alkyl

group, are white powders, practically tasteless and odourless, generally sparingly soluble in water, and of value as anthelmintic remedies. *p*-Benzylphenyl carbamate, crystals (from alcohol), m. p. 144°, is specifically claimed. *p*-Butylphenyl carbonate melts at 108°, *p-iso*amylphenyl carbamate at 73—74°, *p*-butylphenyl carbamate at 123—124°, *p-iso*propylphenyl carbamate at 93—95°, *p*-butylphenyl *N*-dimethylcarbamate at 92°, and *o*-allylphenyl carbamate at 122—123°. A. S.

Synthesis of 3 : 4-Dihydroxyphenanthrene (Morphol) and of 3 : 4-Phenanthraquinone. GEORGE BARGER (T., 1918, **113**, 218—221).—3-Phenanthrol-4-aldehyde (A., 1916, i, 487) dissolved in pyridine reacts vigorously with hydrogen peroxide and potassium hydroxide to form morphol in excellent yield. The method is a modification of Dakin's process for converting *o*- and *p*-hydroxy-aldehydes into dihydric phenols (P., 1909, **25**, 194). The oxidation of morphol to 3:4-*phenanthraquinone* may be achieved by means of dry silver oxide in ether.

For experimental details, see the original. J. C. W.

Preparation of Condensation Products from Aromatic Hydroxysulphonic Acids. BADISCHE ANILIN & SODA-FABRIK (D.R.-P., 301451; addition to 300567; from *Chem. Zentr.*, 1917, i, 787).—Phenolic mono- or di-alcohols are condensed with aromatic hydroxysulphonic acids, or with aromatic hydroxy-compounds followed by sulphonation of the products. For example, *β*-naphthol-6-sulphonic acid is condensed with *p*-homosaligenin, *p*-cresol with *p*-cresoldialcohol (the product has m. p. 215°), and 2-chloro-*α*-naphthol with *p*-homosaligenin and dihydroxyditolylmethane (m. p. 126°; from formaldehyde and *p*-cresol).

J. C. W.

Condensation of Unsaturated Systems. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 932—939).—In addition to the matter referred to in A, 1917, i, 685, this paper contains a description of *β-phenyltrimethylene glycol* (*αγ-dihydroxycumene*),

$$CHPh(CH_2 \cdot OH)_2.$$

This is formed to the extent of 70%, together with some polymeric styrene, by the action of formaldehyde on styrene, $CHPh:CH_2 + H \cdot COH + H_2O = CHPh(CH_2 \cdot OH)_2$. It is a colourless oil, b. p. 145°/12 mm. When heated with acetic anhydride, it is converted quantitatively into the *acetate*, $CHPh(CH_2 \cdot OAc)_2$, b. p. 178°/12 mm.

Preparation of *β*-Naphthyl Benzoate. ANTHONY-HAMMOND CHEMICAL WORKS (U.S. Pat. 1254970).—One hundred and ten grams of *β*-naphthol are heated, and about 170 grams of benzoyl chloride are stirred in, drop by drop, any of the benzoyl chloride which is volatilised being condensed and returned, whilst the hydrogen chloride formed is allowed to escape. A. S.

Preparation of 6-Amino-3-sulphobenzoic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 296941; from *Chem. Zentr.*, 1917, i, 717).—Anthranilic acid is directly sulphonated by means of chlorosulphonic acid in an indifferent solvent, such as nitrobenzene, dichlorobenzene, or petroleum. J. C. W.

***m*-Nitrocinnamic Acid, Brominated in the Side Chain.** S. REICH [with AGAMIRIAN, S. KOEHLER, J. GAJKOWSKI, and (MLLE.) E. LUBECK] (*Arch. Sci. phys. nat.*, 1918, **45**, 191—216, 259—276).—A more detailed account of work already published (compare A., 1914, i, 41). The following additional compounds are described.

The acid described as β-bromo-*m*-nitrocinnamic acid, m. p. 177—179°, has m. p. 184°, and is really the *allo*-acid, giving a *methyl* ester, m. p. 100—101°, and being converted by the action of light into a stable *stereoisomeride*, m. p. 132°, giving a *methyl* ester, m. p. 75—76°.

α-Bromo-*m*-nitro*allo*cinnamic acid when reduced in aqueous barium hydroxide solution with ferrous sulphate yielded a *compound*, brown needles, m. p. 206°. The *isomeride*, m. p. 217°, when similarly reduced, yielded m-*aminophenylpropiolic acid*, $NH_2\cdot C_6H_4\cdot C\colon C\cdot CO_2H$, m. p. 183°. On bromination, α-bromo-*m*-nitro*allo*cinnamic acid yielded *ααβ-tribromo-β-*m*-nitrophenylpropionic acid*, $NO_2\cdot C_6H_4\cdot CHBr\cdot CBr_2\cdot CO_2H$, m. p. 157°, giving a *methyl* ester, m. p. 107—110°. On warming with aqueous sodium carbonate, this acid yielded *ββ-dibromo-*m*-nitrostyrene*, m. p. 58°, which on bromination gave *αβββ-tetrabromo-*m*-nitrophenylethane*, $NO_2\cdot C_6H_4\cdot CHBr\cdot CBr_3$, m. p. 87°. β-Bromo-*m*-nitrocinnamic acid on bromination yielded *αββ-tribromo-β-*m*-nitrophenylpropionic acid*, m. p. 165°, giving a *methyl* ester, m. p. 94—95°.

Attempts to esterify *m*-nitrophenylpropiolic acid by the action of hydrogen chloride in the presence of methyl alcohol yielded *methyl β-chloro-*m*-nitrocinnamate*, m. p. 113—114°.

The cuprous derivative of *m*-nitrophenylacetylene (*loc. cit.*), like the derivatives of phenylacetylene and *o*-nitrophenylacetylene, is oxidised by potassium ferricyanide, giving *dinitrophenyldiacetylene*, $NO_2\cdot C_6H_4\cdot C\colon C\cdot C\colon C\cdot C_6H_4\cdot NO_2$, m. p. 149—150°, which gives a *tetrabromo*-derivative, m. p. 160—161°. *m*-Nitrophenylacetylene when brominated in chloroform solution gave a mixture of cis-*αβ-dibromo-*m*-nitrostyrene*, m. p. 50—51°, and its trans-*isomeride*, m. p. 79°. These two isomerides on further bromination yielded *ααββ-tetrabromo-*m*-nitrophenylethane*,

$$NO_2\cdot C_6H_4\cdot CBr_2\cdot CHBr_2,$$

m. p. 96—97°. This compound or its isomeride (see above) when treated in alcoholic solution with the theoretical quantity of potassium hydroxide yielded *αββ-tribromo-*m*-nitrostyrene*, m. p. 90°.

cis-αβ-Dibromo-*m*-nitrocinnamic acid, m. p. 135—136°, gave a *methyl* ester, m. p. 88°, and its *trans*-isomeride gave a *methyl* ester, m. p. 118—119°.

ω-Bromo-*m*-nitrostyrene has m. p. 76—77°, and not 59° as previously given (*loc. cit.*), and during its formation from αβ-dibromo-*m*-nitrophenylpropionic acid there is produced at the same time some m-*nitrobenzoylacetic acid*,

$$NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2H,$$

m. p. 150°. The bromonitrostyrene on bromination in chloroform solution yielded *tribromo*-m-*nitrophenylethane*,

$$NO_2\cdot C_6H_4\cdot CHBr\cdot CHBr_2,$$

m. p. 86—87°. W. G.

Preparation of Methyl *o*-**Acetoxybenzoate.** L. THORP (U.S. Pat. 1255950).—Methyl salicylate is heated with acetic anhydride in the presence of alkali acetate for ten to twenty hours at 90—100°, then alcohol is added, followed by water until a turbidity is produced, and, after cooling, the ester is collected. A. S.

Normal Ammonium Salts of Organic Acids and their Substituted Derivatives. VII. LE ROY MCMASTER and LETA WRIGHT (*J. Amer. Chem. Soc.*, 1918, **40**, 683—693. Compare A., 1913, i, 248, 444; 1914, i, 481, 1122; 1915, i, 958; 1916, i, 707).—An account of several more *ammonium* salts, prepared by the action of ammonia gas on the acids in anhydrous solvents.

The 2-*hydroxy*-m-*toluate*, 4-*hydroxy*-m-*toluate*, and 3-*hydroxy*-p-*toluate* crystallise in cotton-like masses, and are non-hygroscopic and comparatively stable; the 2:4-*dihydroxybenzoate* is pale pink, and the 2:5-*dihydroxybenzoate* is white; the 2:4-*dinitrobenzoate* is insoluble in most organic media, except methyl alcohol; the *o*-, *m*-, and p-*nitrocinnamates* are not hygroscopic and only sparingly soluble in water; the α- and β-*naphthoates* begin to decompose at 50°. The *m*-nitrobenzenesulphonate; the m-*aminobenzenesulphonate*, large, dark red plates; the α-*naphthylamine-4-sulphonate*, red and blue fluorescence in water; and the α-*naphthol*-4- and -5-*sulphonates*, unstable, brown powders, are described. The *benzilate* forms yellow granules; the oxanilate crystallises in slender needles, and the *phenylpropiolate* is a white powder. J. C. W.

Preparation of Derivatives [Esters] of *iso*Valeric Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (Brit. Pat. 113983).—The esters are prepared by the interaction of hydroxy-fatty acids (for example, glycollic and lactic acids or acids containing an aryl group, such as mandelic acid) and *iso*valeric acid, halogen*iso*valeric acids, especially α-bromo*iso*valeric acid, *iso*valeric anhydride, or *iso*valeryl chloride; or of *iso*valerates and the halogen fatty acids or their salts. They may be neutralised with inorganic or organic bases. The preparation of iso*valerylmandelic* [iso*valeryloxyphenylacetic*] *acid*, m. p. about 71°, both from *iso*valeryl chloride and from *iso*valeric acid, and of its calcium salt and its quinine salt,

m. p. 140°, of its α-bromo-derivative and of *isovalerylglycollic* [*isovaleryloxyacetic*] *acid*, m. p. 46—47°, both from glycollic acid and from sodium chloroacetate, is described. A. S.

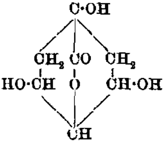
Preparation of an ω-Dihalogeno-*p*-toluoyl-*o*-benzoic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 297018; *from* *Chem. Zentr.*, 1917, i, 715—716).—When 2-*p*-toluoylbenzoic acid is treated with bromine at a high temperature, it is smoothly converted into 2-ω-*dibromo*-p-*toluoylbenzoic acid* (4-*dibromomethyl-2′-carboxybenzophenone*), a white powder, valuable as a source of anthraquinone derivatives, which changes into 4-*aldehydo-2′-carboxybenzophenone* [2-p-*aldehydobenzoylbenzoic acid*] on heating with dilute alkali hydroxides. J. C. W.

The Phenylsuccinic Acid Series. VI. Racemisation Phenomena Observed during the Investigation of the Optically Active Phenyl- and Diphenyl-succinic Acids and their Derivatives. HENRY WREN (T., 1918, **113**, 210—218).—Since the esters of *r*-diphenylsuccinic acid are convertible into the esters of the *meso*-acid (this vol., i, 17), the same should be true of the optically active esters. The truth of this has been experimentally proved by the conversion of methyl and ethyl *l*-diphenylsuccinates into the *meso*-compounds by treatment with solutions of the appropriate sodium alkyloxides, and of ethyl *d*- and methyl *l*-diphenylsuccinates into *meso*-esters during partial hydrolysis.

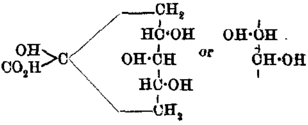
It appears, therefore, that the considerable racemisation which occurs during the hydrolysis of these esters (A., 1915, i, 1061) is mainly due to rearrangement of the esters themselves, and not of the free acids. In this connexion, the more soluble *d*-phenylsuccinates have now been examined. The active methyl and ethyl esters are found to be rapidly and completely racemised by treatment with solutions of the alkyloxides, whilst the free *l*-phenylsuccinic acid is not appreciably affected. The portion of active ester which escapes hydrolysis when submitted to the action of insufficient potassium hydroxide dissolved in slightly diluted alcohol is also extensively racemised. Water has an influence on the extent of the racemisation, for the acid formed by complete hydrolysis with aqueous-alcoholic potassium hydroxide has a much higher rotation the greater the proportion of water in the agent.

The tendency in recent years is to explain racemisation in the case of such esters on the basis of keto-enol desmotropy (see Frankland, T., 1913, **103**, 725). No direct evidence of the usual kind has been obtained in the present case of the formation of sodium enolates, but, inasmuch as the strength of the alkali would have an influence on the extent of the enolisation, it is interesting to record that tetramethylammonium hydroxide causes even more complete racemisation of methyl *d*-phenylsuccinate than potassium hydroxide. J. C. W.

Constitution and Spatial Formula of Quinic Acid. HERMANN EMDE (*Apoth. Zeit.*, 1917, **32**, 601—602; from *Chem. Zentr.*, 1918, i, 208).—From the known physical properties of quinic acid, the author draws the conclusion that the substance is 1:3:4:5-tetrahydroxyhexahydrobenzoic acid. Quinide is the δ-lactone (I), and *l*-quinic acid is represented by the formula II.



(I.)



(II.)

J. C. W.

Hydrosulphonic Derivatives of Citral. GIOVANNI ROMEO (*Gazzetta*, 1918, **48**, i, 45—52. Compare Tiemann and Lemme, A., 1899, i, 248).—With sodium hydrogen sulphite, citral forms the following compounds. (1) The normal compound,

$CMe_2:CH\cdot CH_2\cdot CH_2\cdot CMe:CH\cdot CH(OH)\cdot SO_3Na$,

obtained in presence of a sufficient quantity of free acid, for instance, acetic acid, is crystalline and yields citral when treated with sodium hydroxide solution. (2) The stable dihydrosulphonic derivative, $C_9H_{17}(SO_3Na)_2\cdot CHO$, formed quantitatively when the normal compound is left for some hours in contact with sodium hydrogen sulphite solution maintained acid in reaction, is highly deliquescent, contains the aldehyde group unchanged, and is not decomposed by alkali hydroxide, even in the hot. Its constitution is represented by one of the four formulæ:

$SO_3Na\cdot CMe_2\cdot[CH_2]_3\cdot CMe(SO_3Na)\cdot CH_2\cdot CHO$,
$CHMe_2\cdot CH(SO_3Na)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH(SO_3Na)\cdot CHO$,
$SO_3Na\cdot CMe_2\cdot[CH_2]_3\cdot CHMe\cdot CH(SO_3Na)\cdot CHO$,

and $CHMe_2\cdot CH(SO_3Na)\cdot CH_2\cdot CH_2\cdot CMe(SO_3Na)_2\cdot CHO$. (3) The labile dihydrosulphonic derivative, $C_9H_{17}(SO_3Na)_2\cdot CHO$, formed quantitatively when aqueous sodium hydrogen sulphite is shaken with citral and the alkali neutralised as it is formed, is crystalline and of neutral reaction, and is decomposed by alkali into citral and sodium hydrogen sulphite; by mineral or organic acids, it is slowly transformed into the stable modification. Its structure corresponds with one of the four formulæ given for the stable form. (4) Sodium citraldihydrosulphonate, $C_9H_{16}(SO_3Na)\cdot CHO$, formed from citral and the labile dihydrosulphonate, is a solid, and immediately yields citral when treated in aqueous solution with potassium hydroxide. (5) Labile sodium citraltrihydrosulphonate, $C_{10}H_{19}O(SO_3Na)_3$, *obtained from* citral, sodium sulphite, and sodium hydrogen sulphite, is odourless, non-deliquescent, and of

neutral reaction, and is accompanied by a small proportion of (6), an isomeride stable towards potassium hydroxide.

T. H. P.

Preparation of β-Aminoanthraquinone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1255719).—β-Anthraquinonemonosulphonic acid is heated with ammonia and an aromatic nitro-compound, yielding β-aminoanthraquinone and the amino-compound corresponding with the nitro-compound used. A. S.

Crystallographic and Optical Characters of Amyrolin. HERMANN ROSE (*Jahrb. Min.*, 1918, 1—18).—Amyrolin, $C_{14}H_{12}O_3$ (von Soden and Rojahn, A., 1901, i, 159), has D^{18} 1·351 and m. p. 119—124°. The crystals are monoclinic, $a:b:c = 0·7583:1:1·1106$; $\beta = 76°55'$. The optical constants are given for wave-lengths 690·7 to 404·7 $\mu\mu$. For sodium light, $\alpha = 1·46447$, $\beta = 1·74798$, $\gamma = 1·94579$, $\gamma - \alpha = 0·48132$. The dispersion and double refraction are high, the latter being exceeded only by that of calomel.

L. J. S.

Gossypol, the Toxic Principle of Cotton Seed. FRANK E. CARRUTH (*J. Amer. Chem. Soc.*, 1918, **40**, 647—663).—Gossypol is a colouring matter of phenolic nature occurring in glands in the seeds and in all parts of the cotton plant except the woody tissues. It is the toxic substance of cotton seed (compare A., 1917, i, 719). It may be precipitated as a compound with acetic acid or aniline by adding these agents to ethereal extracts of cotton seed. The first compound is decomposed by dissolving in ether, mixing with water, and distilling the solvent, when free gossypol separates on the surface, and the aniline salt is decomposed by hot alcoholic potassium hydroxide, the solution being then submitted to a current of steam and finally acidified.

Present analyses of gossypol, and molecular weight determinations, agree with the formula $C_{30}H_{28}O_9$ or $C_{30}H_{30}O_9$. The *compound* with acetic acid (1 mol.) corresponds with Marchlewski's gossypol (A., 1899, i, 821). A similar unimolecular *compound* with acetone, a *tetra-* or *penta-acetate* and *-benzoate*, a very sparingly soluble, orange-yellow *aniline* salt (2 mols. to $5NH_2Ph$?), and some metallic salts are described.

When heated at 186—190°, gossypol decomposes into a black mass, from which ether extracts a sparingly soluble, intensely yellow substance, m. p. 246—248°, termed B-*gossypol*. It is much less toxic than gossypol. Fusion with alkali hydroxide, followed by acidification in the presence of sodium hyposulphite (to prevent oxidation), gives a white product, C-*gossypol*. Cotton-seed meal, obtained by cooking the seeds for the oil, does not contain much gossypol as such, but D-gossypol (*loc. cit.*) instead. All four products behave alike in giving blood-red solutions in concentrated sulphuric acid and blue colorations when their alkaline solutions are exposed to the air. [See also *J. Soc. Chem. Ind.*, 319A.]

J. C. W.

Analogues of Atropine and Homatropine. LOUIS F. WERNER (*J. Amer. Chem. Soc.*, 1918, **40**, 669—674).—When tropinone (I) is reduced by means of hydriodic acid, or electrolytically, it yields tropine, the tropate and mandelate of which are the well-known mydriatics atropine and homatropine. If reduced by means of sodium and alcohol, however, it gives ψ-tropine, the hydroxy-acid esters of which are not physiologically active. The alkaloid of the pomegranate, ψ-pelletierine (II), is a homologue of tropinone, and this also gives two isomerides on reduction.

(I.) (II.)

When treated with sodium and alcohol, it yields the alkamine, methylgranatoline (Ciamician and Silber, A., 1894, i, 154); the *hydrobromide* of the *tropate* of this, m. p. 220°, and the *hydrobromide* of the *mandelate* are powerful mydriatics. Reduction with hydriodic acid and zinc dust at 0° gives *isomethylgranatoline*, m. p. 65°; the *tropate hydrobromide*, m. p. 233°, and *mandelate hydrobromide*, m. p. 229°, of this are inactive. Compared with the tropines, therefore, the products formed by like methods of reduction give esters of opposite physiological effects. J. C. W.

Preparation of Homologues of Emetine. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 301498; from *Chem. Zentr.*, 1918, i, 53).—Cephaeline is converted into its ethyl, propyl, and *benzyl* ethers. (Compare Karrer, A., 1916, i, 833, and Meader, *ibid.*, 834.) J. C. W.

The supposed Formation of Ergotoxine Ethyl Ester from Ergotinine. A Correction. GEORGE BARGER and ARTHUR JAMES EWINS (T., 1918, **113**, 235—238).—The phosphate obtained by boiling ergotinine in alcoholic solution with phosphoric acid is the salt of ergotoxine itself and not of its ethyl ester, as was originally supposed (T., 1910, **97**, 284). From the results of Zeisel determinations, the authors are inclined to believe that ergotoxine and ergotinine contain one *N*-methyl group, but no methoxy-group. J. C. W.

The Alkaloids of Ipecacuanha. III. FRANK LEE PYMAN (T., 1918, **113**, 222—234. Compare A., 1917, i, 410).—In the last communication it was shown that *O*-methylpsychotrine yields emetine and *iso*emetine on reduction. The formation of the latter isomeride was demonstrated by the isolation of its previously known benzoyl derivative; it is now confirmed by the actual separation of the base itself, some characteristic salts of which are described. On oxidation, *iso*emetine, like emetine, may be converted into *O*-methylpsychotrine or rubremetine, which shows

that the two bases are stereoisomerides. Equilibrium between them could not be established, however, by boiling with sodium and amyl alcohol. *iso*Emetine is rather less than half as toxic as emetine.

Psychotrine itself yields cephaeline and *iso*cephaeline on reduction, and, as might be expected, the latter may be converted into *iso*emetine by methylation. *iso*Emetine may be transformed under suitable conditions into *N*-methyl*iso*emetine, and this may also be formed by methylating *N*-methyl*iso*cephaeline (T., 1914, **107**, 1624).

N-Methyl*iso*emetine has also been completely methylated, the product being a mixture of a crystalline and an amorphous methiodide, apparently stereoisomerides, since they yield the same *N*-methyl*iso*emetine methine when the methohydroxides are heated. In the same way, emetine itself forms two *N*-methylemetine methiodides, which yield the same methine.

For details, the original should be consulted, where a chart showing the relationships between the ipecacuanha alkaloids, established experimentally by the author, will be found. J. C. W.

Relative Stability of Cyclic Bases. VI. The Morpholine Ring. J. von Braun and Z. Köhler (*Ber.*, 1918, **51**, 255—265. Compare this vol., i, 185).—The authors have established the order of stability of a number of cyclic bases under the disruptive influence of cyanogen bromide and in the Hofmann reaction. It is now found that the morpholine system is to be placed along with tetrahydro*iso*quinoline and dihydro*iso*indole among the bases which are most easily ruptured by cyanogen bromide, and between these two in stability during the Hofmann reaction.

1-Methylmorpholine (I) (Knorr, A., 1898, i, 602) reacts very vigorously with cyanogen bromide diluted with ether, giving a crystalline precipitate of the hydrobromide of the base mixed with a trace of an undefined compound, $C_8H_{12}ON_5$, and a solution which contains an unstable oil (II). This condenses with piperidine to form *β-cyanomethylaminoethyl β-1-piperidinoethyl ether* (III), b. p. 170—175°/30 mm., which forms a *platinichloride*, stout, red, tablets, m. p. 166°, and a *picrate*, m. p. 139—140°. The main reactions are therefore represented by the scheme:

$$NMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>O \text{ (I.)} \xrightarrow{BrCN} CN\cdot NMe\cdot C_2H_4\cdot O\cdot CH_2\cdot CH_2Br \text{ (II)}$$

$$\downarrow$$

$$CN\cdot NMe\cdot C_2H_4\cdot O\cdot CH_2\cdot CH_2\cdot N:C_5H_{10} \text{ (III.)}$$

In order to compare the stability of the morpholine ring with the tetrahydro*iso*quinoline system under the conditions of the Hofmann reaction, a compound with a nitrogen atom common to both rings has been prepared. This is the *quaternary ammonium iodide*, $\begin{matrix}CH_2-CH_2\\C_6H_4\cdot CH_2\end{matrix}>\underset{I}{N}<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>O$, which is obtained by mix-

ing tetrahydro*iso*quinoline, $\beta\beta'$-di-iodoethyl ether, and 10% aqueous sodium hydroxide. It is a pale yellow, crystalline salt, m. p. 214—215°, and the corresponding *platinichloride* has m. p. 230°. When the iodide is converted into the hydroxide and this is distilled under reduced pressure, the main product is 1-o-*vinylbenzylmorpholine*, $CH_2:CH\cdot C_6H_4\cdot CH_2\cdot N<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>O$, which boils at 138—142°/6 mm., with partial polymerisation, and forms a *hydrochloride*, m. p. 211°, a *platinichloride*, red needles, m. p. 186°, a *picrate*, m. p. 164°, and a *methiodide*, m. p. 155—156°. The base combines with hydrogen bromide in concentrated solutions, forming an oily *bromide* (IV), which soon changes into the stable *quaternary bromide* (V), this having m. p. 213—215°, and yielding the corresponding red *platinichloride*, m. p. 220—223°. It may

$$CH_3\cdot CHBr\cdot C_6H_4\cdot CH_2\cdot N<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>O \longrightarrow$$

(IV.)

$$C_6H_4<^{CHMe}_{CH_2\text{—}}>\underset{Br}{N}<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>O.$$

(V.)

also be reduced to 1-o-*ethylbenzylmorpholine*, a viscous oil, b. p. 138—140°/11 mm. (*picrate*, m. p. 142°; *platinichloride*, m. p. 189°), which reacts with cyanogen bromide to form *o*-ethylbenzyl bromide (A., 1917, i, 259). These reactions of the base are sufficient evidence that it is 1-*o*-vinylbenzylmorpholine; in other words, that it is the tetrahydro*iso*quinoline ring, and not the morpholine ring, which is ruptured when the quaternary ammonium hydroxide is heated.

For a comparison between the morpholine and dihydro*iso*indole systems, morpholine, *o*-xylylene dibromide, and 10% sodium hydroxide are warmed together, the quaternary ammonium bromide so formed is converted into the hydroxide (VI) (*platinichloride*, m. p. 225°; *aurichloride*, m. p. 147°), and this is distilled. The chief product is 2-β-*vinyloxyethyldihydro*iso*indole* (VII), which has b. p. 176—180°/12 mm., and yields a *picrate*, m. p. 105°, and

$$C_6H_4<^{CH_2}_{CH_2}>\underset{OH}{N}<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>O \longrightarrow C_6H_4<^{CH_2}_{CH_2}>N\cdot C_2H_4\cdot O\cdot CH:CH_2$$

(VI.) (VII.)

a *methiodide*, m. p. 129°. Consequently, the morpholine ring is the weaker in this case. J. C. W.

Bromoalkylated Aromatic Amines. II. J. von Braun, K. Heider, and E. Müller (*Ber.*, 1918, **51**, 273—282. Compare this vol., i, 107).—Some further reactions of methyl-β-bromoethylaniline are described, as well as the application of other secondary amines and ethylene dihaloids to the production of similar bromoalkylated bases.

When methyl-β-bromoethylaniline is heated with formaldehyde and hydrobromic acid, it yields *dimethyldi-β-bromoethyldiamino-*

diphenylmethane, $CH_2(C_6H_4\cdot NMe\cdot C_2H_4Br)_2$, which crystallises in colourless leaflets, m. p. 115—116°. If hydrochloric acid is used, the bromine is replaced and *dimethyldi-β-chloroethyldiaminodiphenylmethane*, m. p. 97—98° (*picrate*, m. p. 147°) is formed.

With potassium phthalimide at 145—150°, the base reacts vigorously, forming *methyl-β-phthalimidoethylaniline*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_2H_4\cdot NMePh,$$

in canary-yellow, glistening leaflets, m. p. 109°; *methiodide*, m. p. 165°. The potassium salt of "saccharin" yields the corresponding *β-benzoicsulphinidoethylmethylaniline*,

$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot C_2H_4\cdot NMePh,$$

as a pale yellow, glistening mass, m. p. 115°, which forms an extremely bitter *methiodide*, m. p. 150°, and a p-*nitroso*-compound, a green powder, m. p. 190°, from which the p-*amino*-derivative, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot C_2H_4\cdot NMe\cdot C_6H_4\cdot NH_2$, *may be obtained as a* reddish-yellow powder, m. p. 111—112°. The "saccharin" derivative yields a flocculent diphenylmethane compound when heated with formaldehyde in the usual way. The hydrol obtained on oxidation with lead peroxide has a pure green colour in acid solutions, instead of the usual blue. To decide whether this difference is characteristic of the benzoicsulphinide group, a number of typical dyes (not described) have been prepared with this *tert.*-amine instead of a simple dialkylaniline, and in only one other case has an abnormally coloured product been obtained, namely, the compound related to methylene-blue, which is dark green.

Methylaniline reacts with *s*-chlorobromoethane under the conditions suitable for the production of methyl-β-bromoethylaniline to form a mixture of this with methyl-β-chloroethylaniline in almost equivalent quantities, having b. p. 116—120°/3 mm.

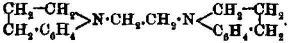
Ethylaniline and ethylene dibromide yield a mixture of diphenyldiethylethylenediamine, $C_2H_4(NEtPh)_2$, b. p. 223°/16 mm., and *β-bromodiethylaniline*, $NEtPh\cdot CH_2\cdot CH_2Br$. The latter is a pale yellow oil, b. p. 151—154°/15 mm., which forms a *picrate*, m. p. 95°, and resembles methyl-β-bromoethylaniline in all its activities. For example, it reacts with sodium to give *diphenyldiethyltetramethylenediamine*, $C_4H_8(NEtPh)_2$, b. p. 234—236°/12 mm.; *picrate*, m. p. 190°.

Methyl-*o*-toluidine and a large excess of ethylene dibromide, after heating for twenty-four hours, give a mixture of bases which are divided by distillation into (1) unchanged base, 20% of the weight of the base, (2) a fraction with b. p. 100—190°/6 mm., 40%. and (3) a fraction with b. p. about 200°/6 mm., 48%. The second fraction is freed from unchanged base by converting this into its nitroso-compound, and then yields on redistillation *methyl-β-bromoethyl-o-toluidine*, b. p. 118—120°/5 mm., which forms a *picrate*,

m. p. 90°, and reacts with trimethylamine to give the *quaternary bromide*, $C_6H_4Me{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$, glistening leaflets, m. p. 173—174°. The third fraction is mixed with trimethylamine to remove any bromoalkylated base as the foregoing salt, and then *di*-o-*tolyldimethylethylenediamine*, $C_2H_4(NMe{\cdot}C_6H_4Me)_2$, is recovered as a hard mass, m. p. 46—47°, b. p. 199—201°/6 mm., which forms a *picrate*, m. p. 178°, and a *dibromide*, m. p. 88°.

Methyl-α-naphthylamine also yields a bromoalkylated base when heated with ethylene dibromide, but it decomposes on distillation. The parent substance is obtained as follows. The dimethyl-α-naphthylamine of commerce is warmed with cyanogen bromide, which yields *α-naphthyltrimethylammonium bromide*, m. p. 160°, insoluble in ether, and *cyanomethyl-α-naphthylamine*, $C_{10}H_7{\cdot}NMe{\cdot}CN$, a yellow oil, b. p. 189—191°/5 mm., soluble in ether, and the latter is hydrolysed to methyl-α-naphthylamine by boiling with 20% hydrochloric acid.

Tetrahydroquinoline and ethylene dibromide yield, chiefly, crystalline s-1 : 1-*ditetrahydroquinolylethane*,



J. C. W.

Ethyl*iso*propylbarbituric Acid. L. THORP (U.S. Pat. 1255951). —Ethyl*iso*propylbarbituric acid, prepared by the usual methods, forms snow-white crystals (from water), m. p. 197—198°, has a faint, bitter taste, and is readily soluble in alcohol or ether. The acid and its alkali salts, which are readily soluble in water, possess marked hypnotic and sedative powers, and are relatively devoid of toxic action. A. S.

Compounds derived from Diallylbarbituric Acid and Alkaloids of the Morphine Series and Process of making same. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1255423, 1918; from *J. Soc. Chem. Ind.*, 1918, **37**, 193A. Compare A., 1917, i, 664).—The compound formed by diallylbarbituric acid and ethylmorphine is a white, crystalline substance, m. p. 285°. The compounds generally are easily soluble in hot water, methyl or ethyl alcohol, acetone, or ethyl acetate, but insoluble in light petroleum. H. M. D.

Preparation of Phenylethylbarbituric Acid. MARY RISING and JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1918, **40**, 723—730). —Some practical notes on the preparation of the necessary intermediate compounds and on the final stages in the synthesis of phenylethylbarbituric acid. This compound, which was introduced as a specific in cases of epilepsy under the name "luminal," is officially designated "phenylbarbital" in America, as veronal is termed "barbital." [See, further, *J. Soc. Chem. Ind.*, 322A.] J. C. W.

Preparation of Nitrogenous Vat Dyes of the Anthracene Series. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P., 301554; from *Chem. Zentr.*, 1918, i, 150).—The yellow vat dye obtained by the action of concentrated alcoholic alkali hydroxide on pyrazole-anthrone (A., 1913, i, 533) forms alkali salts which react with the usual alkylating agents. The alkyl derivatives so formed are much deeper in colour than the parent dye; for example, the *benzyl* compound is scarlet, and the *ethyl* derivative, Bordeaux-red.

J. C. W.

Halogenated Dyes of the Acridine Series. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (U.S. Pat. 1255739).—A new acridine dye obtained by heating chloroformyl-*m*-phenylene-diamine ($NH_2:NH\cdot CHO:Cl=1:3:6$) with *m*-phenylenedimethyl-diamine hydrochloride, is a brownish-black powder which dyes leather reddish-yellow. The patent covers derivatives of dyes of the general formula $NH_2\cdot C_6H_3<\overset{N}{\underset{CH}{|}}>C_6H_3\cdot NR_1R_2$, in which R_1 and R_2 represent univalent substituents, including hydrogen, and one or more hydrogen atoms of the benzene nuclei have been displaced by halogen.

A. S.

Acridine Dyes of the Benzene-naphthalene Series. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (U.S. Pat. 1255740).—A new acridine dye of the formula:

$$\begin{matrix}(2)CH_3 \\ (3)(CH_3)_2N\end{matrix}>C_6H_2<\overset{N}{\underset{CH}{|}}>C_{10}H_6$$

is a reddish-brown powder, which dyes leather in deep orange-yellow shades. The patent covers dyes of the general formula $R_2R_1N\cdot C_6H_2<\overset{N}{\underset{CH}{|}}>C_{10}H_6$, obtained by heating a formyl derivative of β-naphthylamine with a salt of a *m*-diamine of the benzene series.

A. S.

Preparation of Condensation Products of Isatin and Ketones. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P., 301591; from *Chem. Zentr.*, 1918, i, 148—149).—Condensation products, of unexplained nature, are obtained by mixing acetophenone or its derivatives with isatin and ammonia solution. Acetophenone itself gives a pale yellow *product*, $C_{16}H_{12}O_3N$ [?], m. p. 152—153°; *p*-tolyl methyl ketone yields a white *product*, m. p. 165—167°; deoxybenzoin forms a *product*, m. p. 147°; and the *product* from 3-nitro-4-hydroxyacetophenone forms yellow crystals, m. p. 191°.

J. C. W.

Preparation of Mono-azo-dyes suitable for Pigment Manufacture. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 296991; from *Chem. Zentr.*, 1917, i, 718).—Diazotised 1-amino-anthraquinone is coupled with 1-benzoylamino-7-hydroxynaphth-

alene, or the substituted benzoylamino-analogues, in the presence of Turkey-red oil, or such substances, with or without a substrate.

The 8-benzoylamino-β-naphthols employed are mostly colourless, crystalline compounds. The following are mentioned: *8-benzoylamino-β-naphthol*, m. p. 208—209°; 8-o-*chlorobenzoylamino-β-naphthol*, m. p. 158—160°; 8-p-*chlorobenzoylamino-β-naphthol*, m. p. 230—231°; 8-op-*dichlorobenzoylamino-β-naphthol*, m. p. 186—187°; 8-2′:6′-*dichlorobenzoylamino-β-naphthol*, m. p. 230—232°; 8-o-*nitrobenzoylamino-β-naphthol*, m. p. 227—228°; 8-m-*nitrobenzoylamino-β-naphthol*, m. p. 204—205°; 8-p-*nitrobenzoylamino-β-naphthol*, m. p. 255—260° (decomp.). J. C. W.

Preparation of Acid Mono-azo-dyes for Wool. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296964; from *Chem. Zentr.*, 1917, i, 717).—Good dyes which colour wool yellow to bluish-red or brown shades in acid baths are obtained by coupling pyrazolone-, methylketol-, α- or β-naphthol-, or 8-acylamino-α-naphthol-sulphonic acids with diazotised phenylenediamines of the type $NH_2{\cdot}R''{\cdot}NRR'$, where R = alkyl or aryl, R′ = an aromatic acyl group, such as Bz or $OMe{\cdot}C_6H_4{\cdot}CO$, and R″ = the benzene nucleus or a homologue or substituted nucleus. The necessary bases are obtained by treating alkylated or arylated anilines with benzoyl chloride or substituted benzoyl chlorides, nitrating the products, and then reducing the nitro-compounds.

Thus, ethylaniline, after benzoylation, nitration, and reduction, yields *benzoylethyl*-p-*phenylenediamine*, $NH_2{\cdot}C_6H_4{\cdot}NEtBz$, m. p. 114°, and methylaniline gives *benzoylmethyl*-p-*phenylenediamine*, m. p. 143°. Benzoylethyl-*m*-toluidine yields *benzoylethyltolylene-2:5-diamine*, m. p. 140°; benzoylethyl-*p*-xylidine yields *benzoylethyl*-p-*xylylene*-2:5-*diamine*, $NH_2{\cdot}C{<}{}^{CH:CMe}_{CMe\cdot CH}{>}C{\cdot}NEtBz$, m. p. 134°; benzoylmethyl-*o*-toluidine gives *benzoylmethyltolylene-2:4-diamine*, m. p. 167°; 2′-chlorobenzoylethylaniline gives *2′-chlorobenzoylethyl*-p-*phenylenediamine*, m. p. 135°; and 4-nitrodiphenylamine yields *benzoylphenyl*-p-*phenylenediamine*, m. p. 178°.

J. C. W.

Preparation of Yeast-nucleic Acid. EMIL J. BAUMANN (*Proc. Amer. Soc. Biol. Chem.*, 1917, xiv.–xv.; *J. Biol. Chem.*, 1918, **33**).—Fresh brewer's yeast is diluted with water and treated with sodium hydroxide solution (100 grams of alkali per kilo. of yeast) in the cold, which separates the nucleoprotein into protein and nucleic acid. Since nucleic acid is soluble in dilute acetic acid, the solution is now partly neutralised with hydrochloric acid and then made acid with acetic acid. The precipitated proteins are removed by filtration and the nucleic acid in the filtrate precipitated by the addition of 5% magnesium sulphate solution and enough hydrochloric acid to cause the separation of the flocculent precipitate. The yield of dry mono-magnesium nucleate is 4 to 7½ grams per kilo. of yeast H. W. B.

Nucleic Acid of the Lymph Corpuscle. R. NAKASAKO (*A. C. James Res. Lab., Bull.*, 1917, No. 3; from *Physiol. Abstr.*, 1918, **3**, 4—5).—The nucleic acid was prepared from lymph glands by a modification of Kossel's method. It closely resembles the thymus acid, and to it the author assigns the formula $C_{41}H_{65-64}O_{25}N_{14}P_4$. Amongst the products of hydrolysis, xanthine, hypoxanthine, guanine, adenine, thymine, and a compound containing either of the groups $CH_3{\cdot}CO{\cdot}C$ and $CH_3{\cdot}CH(OH){\cdot}C$ were identified. The existence of a carbohydrate is uncertain.

W. G.

Effect of Potassium Bromate on Enzyme Action. I. S. FALK and C.-E. A. WINSLOW (*J. Biol. Chem.*, 1918, **33**, 453—462).—Potassium bromate exerts a slight stimulating action on trypsin and pancreatin when it is present in concentrations of 1 part in 100,000 to 1 part in 250,000. With higher concentrations, the proteolytic action is depressed. H. W. B.

Action of Ammonium Compounds on Ptyalin. ELBERT W. ROCKWOOD (*Proc. Amer. Soc. Biol. Chem.*, 1917, ix–x; *J. Biol. Chem.*, 1918, **33**).—Ammonium salts of inorganic and organic acids increase the activity of ptyalin. In general, the ammonium salts of the strong acids have a greater activating effect than those of the weak acids. Ammonium oxalate is an exception, having little or no action. H. W. B.

The Action of Acids on Ricinus Lipase and the Reaction of the Substratum. G. KITA (*J. Chem. Ind., Tokyo*, 1918, **21**, 1—4).—Green and Hoyer have shown that acids have a powerful activating influence on the lipase of castor beans, and that the activated lipase exerts its specific activity in neutral media. Further, lipase which has been rendered active by treatment with acids and thoroughly washed has a more powerful action in faintly acid media than in neutral. The author has found that the activated lipase, which is extremely unstable in presence of acids, becomes comparatively far more permanent in presence of the oil to be hydrolysed. Armstrong overlooked this fact, and considered that the acid played some other part than the liberation of the zymogen, because the quantity of acid which is most favourable to fat hydrolysis was capable under the same conditions of destroying the lipase of de-fatted castor beans. The author considers that, although the activated lipase is again rendered inactive by acids, the simultaneous presence of fat is capable of exerting a protective action on the lipase in the hydrolysis of fats. J. F. B.

The Action of Aldehydes on Urease. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **85**, 358—364).—Aldehydes inhibit the action of urease. The cyanohydrin of acetaldehyde, however (but not that of benzaldehyde) accelerates the action. S. B. S.

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON HEYDEN, AKT.-GES. (D.R.-P., 296940; with 261825 and 269255, an addition to 254421; from *Chem. Zentr.*, 1917, i, 715. Compare A., 1913, i, 416, 1122; 1914, i, 217).—Nitro-derivatives of aromatic stibinic acids are prepared by treating diazotised nitroamines with antimonites or antimonious acid, in acid or neutral solutions, at low temperatures. Antimony trioxide dissolved in such an acid as tartaric acid is recommended, and copper powder is often useful as a catalyst. 2-*Nitro-* and 2:4-*dinitro-phenylstibinic acids* are brown powders which explode on heating. 3-Nitro-*p*-anilinoarsinic acid yields *2-nitro-4-arsinophenylstibinic acid*, $AsO_3H_2 \cdot C_6H_3(NO_2) \cdot SbO_3H_2$, which is a similar brown powder.
J. C. W.

Physiological Chemistry.

The Oxygen and Carbon Dioxide Tension in the Blood of the Pulmonary Artery and the Measurement of the Minute Volume of the Heart. L. S. FRIDRICIA (*Biochem. Zeitsch.*, 1918, **85**, 307—357).—The method of measurement employed by the author is described in detail. It is based on the use of a spirometer constructed by Krogh on the principle of the aeroplethysmograph. It was found that the tensions of oxygen and carbon dioxide in pulmonary blood are not constant in the same individual when in a state of rest. The average values for three persons were 40·7, 44·5, and 35·1 mm. for oxygen and 45·2, 46·3, and 45·2 mm. for carbon dioxide. There are wider variations, therefore, in the oxygen than in the carbon dioxide tensions. During muscular work (200 kg./m. per minute), the ratios of the tensions to the tensions found for the same individual when at rest were for oxygen 35·2 : 44·5, and for carbon dioxide 55·2 : 46·3. The minute volume of the heart was estimated by the methods of Krogh and Lindhard and of Fick, and the two were found to give results which were satisfactorily concordant.
S. B. S.

Comparison of the Dextrose and Cholesterol Content of the Blood. F. H. MCCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1918, **33**, 387—389).—The amounts of dextrose and of cholesterol in the blood in various diseases do not show any kind of parallelism. The association of hyperglycæmia and hypercholesterolæmia in diabetes (Bloor, Joslin, and Hornor, A., 1916, i, 776) is therefore probably due to an indirect physiological relationship.
H. W. B.

Fatty Acids in Human Blood in Normal and Pathological Conditions. FRANK A. CSONKA (*J. Biol. Chem.*, 1918, **33**, 401—409. Compare A., 1916, ii, 349).—The method

previously described for the estimation of fatty acids in fæces (Gephart and Csonka, A., 1915, ii, 74) can be applied in the case of blood, using 5 c.c. of oxalated blood, and the author's saponification and extraction flask (*loc. cit.*). For the estimation of the unsaturated fatty acids, about 100 c.c. of blood are extracted with alcohol and ether, and the extract saponified by the Gephart and Csonka method. The mixed fatty acids are converted into their lead soaps, which are then extracted with ether, which dissolves the lead soaps of the unsaturated fatty acids. The free acids are liberated from the soaps by hydrochloric acid, and, after weighing, the iodine numbers are determined according to Hübl.

The blood of normal individuals contains about 0·14 gram of unsaturated fatty acids per 100 c.c., with an average iodine number of 87·5. The iodine number varies from 76 to 105, thus indicating the presence, in addition to oleic acid, of other both higher and lower unsaturated fatty acids in small amounts. In normal human blood, about one-half of the total fatty acids are unsaturated. In pathological conditions, there is generally a higher proportion of unsaturated fatty acids with higher iodine values, especially in cases where the hæmoglobin content of the blood is low. In such cases, the smaller number of red corpuscles present in the blood reduces the amount of unsaturated fatty acid which can be utilised for metabolic purposes, and this results in an accumulation of unsaturated fatty acids in the blood (compare Bloor, A., 1916, i, 450). H. W. B.

Adsorption Phenomena in Coagulation. G. H. A. Clowes (*Proc. Amer. Soc. Biol. Chem.*, 1917, xx; *J. Biol. Chem.*, 1918, **33**).—The author has determined the effect on the coagulation of blood of the addition of precipitated or colloidal barium sulphate, calcium oxalate, etc., which adsorb prothrombin. The adsorption is proportional to the degree of dispersion of the adsorbent and depends also on the presence of unsaturated lipoids like kephalin. Apparently the physical quality and speed of formation of the blood clot depend on the degree of dispersion of the reacting colloids and on their initial and final concentrations.

H. W. B.

Relation between Phosphorus Metabolism and the Secretion of Milk-fat. Edward B. Meigs and N. R. Blatherwick (*Proc. Amer. Soc. Biol. Chem.*, 1917, iv—v; *J. Biol. Chem.*, 1918, **33**).—Experiments on cows are described in which the distribution of phosphorus in the blood is determined before entering and after leaving the mammary gland. When the cow is disturbed by the operative procedure, the lipoid phosphorus in the blood remains unaltered, but when the cow is quiet, a diminution in the lipoid phosphorus occurs during the passage of the blood through the active gland. In all cases, an increase in the inorganic phosphate in the blood coming from the gland is observed.

The authors consider that the results show that the precursor

in the blood of both milk fat and milk phosphorus is either lecithin or a related compound. The ratio phosphorus : fat in lecithin is about 1 : 18, whereas it is about 1 : 50 in milk. Hence relatively more phosphorus is supplied to the gland than is required for the milk, and the excess is returned to the blood as inorganic phosphate. H. W. B.

Metabolism of α-Carbamido*iso*butylacetic Acid. ALICE KOHDE (*Proc. Amer. Soc. Biol. Chem.*, 1917, xii; *J. Biol. Chem.*, 1918, **33**. Compare A., 1917, ii, 344).—The intravenous injection of α-carbamido*iso*butylacetic acid in saline solution into a cat is followed by the elimination of a considerable proportion of the acid in the urine. The acid is identified by the method previously described in the case of phenylalanine–carbamido-acid (*loc. cit.*). H. W. B.

Endogenous Uric Acid Metabolism. HOWARD B. LEWIS, MAX S. DUNN, and E. A. DOISY (*Proc. Amer. Soc. Biol. Chem.*, 1917, xv—xvi; *J. Biol. Chem.*, 1918, **33**).—The authors describe the influence of the ingestion of proteins and various protein derivatives on the hourly elimination of uric acid in a subject on a purine-free low protein diet. Protein (egg-white, cheese) causes a slight rise, beginning the second hour after the meal and increasing to a maximum at the fourth hour. Ingestion of equivalent amounts of nitrogen in the form of glycine or alanine results in a sharp rise in the second hour, followed by a prompt return to the normal level. Administration of a second portion of glycine following the return to normal causes a like increase in the uric acid excretion. Aspartic and glutamic acids produce eliminations of uric acid of even greater magnitude. Neither urea nor ammonium chloride administered in amounts comparable to the amino-acids has any influence on the output of uric acid. The authors draw the conclusion that the rise in the excretion of uric acid following ingestion of protein food is not due mainly to the work of the digestive glands, but to stimulation of the cellular mechanism by the amino-acids liberated in the digestion of the protein. Creatinine excretion was not affected in any of the experiments. H. W. B.

Rôle of some Inorganic Elements in Nutrition. LAFAYETTE B. MENDEL and THOMAS B. OSBORNE (*Proc. Amer. Soc. Biol. Chem.*, 1917, iii; *J. Biol. Chem.*, 1918, **33**).—The essential factors of a successful dietary having now been ascertained, it has become possible to prepare rations in which the individual ions are excluded except for the unavoidable small amounts present in the products used to supply the water-soluble vitamine or found as impurities in the other ingredients of the food. Experiments with such diets demonstrate that calcium and phosphorus are needed in considerable amounts, for with only a trace of either of these elements in the diet, rats fail to grow and sooner or later decline.

On diets in which one of the elements magnesium, sodium, potassium, or chlorine are absent, growth continues at the normal rate. When both sodium and potassium are absent, growth does not occur. H. W. B.

Formation of Structures Resembling Organic Growths by Electrolytic Action in Metals. R. S. Lillie (*Biol. Bull.*, 1917, **33**, 135—186; from *Physiol. Abstr.*, 1918, **3**, 7—8).—A study of the conditions under which filaments, formed of ferricyanides of iron, zinc, copper, etc., are produced in mixtures of albumin and potassium ferrocyanide. Only those metals the ferricyanides of which form semipermeable membranes exhibit the phenomenon. The author suggests that in organic growth the essential structural condition is possibly the presence of semipermeable, and hence electrically polarised, partitions separating the living substance from its medium, and at which the process of electrolysis may take place. W. G.

Differences in the Swelling of the Plasma Colloids as a Cause of the Invagination of the Gastrula and generally of the Curving and Folding of Layers of Cells. Josef Spek (*Koll. Chem. Beihefte*, 1918, **9**, 259—399).—A paper, mainly of biological interest, in which an attempt is made to show that changes in the geometrical form of certain tissues are due to differences in the extent to which the colloidal constituents of the cells are swollen by the absorption of water. The degree of swelling is appreciably affected by the electrolytes present, and the results of some observations on the swelling of fibrin under the influence of solutions of acids and salts are recorded. These show that for salt concentrations which fall within the physiological range, the effect of the presence of acids is to increase considerably the degree of swelling of the plasma colloids. H. M. D.

Autolysis. H. C. Bradley (*Proc. Amer. Soc. Biol. Chem.*, 1917, xi; *J. Biol. Chem.*, 1918, **33**).—The autolysis of nervous tissue, like muscle and gland tissues, is accelerated by acids and inhibited by alkalis. Striated muscle autolyses more slowly than either cardiac or involuntary muscle. The accelerating action of inorganic hydrosols on the autolysis of liver described by Ascoli and Izar (A., 1909, ii, 501) is not confirmed. H. W. B.

Conjugation of Hippuric Acid. E. Lackner, A. Levinson, and Withrow Morse (*Proc. Amer. Soc. Biol. Chem.*, 1917, xvi—xviii; *J. Biol. Chem.*, 1918, **33**).—After fatty degeneration of the liver has been produced in dogs by the subcutaneous injection of hydrazine, ingestion of sodium benzoate causes a diminished output of hippuric acid compared to that observed in the normal animal. Apparently the kidney is not affected by the hydrazine injection, and therefore the authors draw the conclusion that, normally, conjugation of hippuric acid occurs in the liver. These

results are confirmed by the following clinical observations. In normal children, ingestion of sodium benzoate produces an increased elimination of hippuric acid. A case of a child with diseased liver is described in which administration of sodium benzoate did not have any effect on the output of hippuric acid.

H. W. B.

Creatine Content of Skeletal Muscle in Degeneration following Denervation. E. P. Cathcart, P. S. Henderson, and D. Noël Paton (*J. Physiol.*, 1918, **52**, 70—74).—Up to the eleventh day after section of the nerve there is no distinct change, but after the fifteenth day, when the reaction of degeneration is well established, there is a steady and progressive decrease in the creatine content of muscle, becoming very pronounced (30—60%) between the third and fourth weeks. G. B.

Guanidine Content of Muscle in Tetania Parathyreopriva. Pearl S. Henderson (*J. Physiol.*, 1918, **52**, 1—5).—Removal of the parathyroids causes a fall in the total and in the free guanidine of muscle and a rise in the creatine content corresponding fairly closely with the fall in free guanidine. The fall in total guanidine is, however, so great that it may be correlated with the increase in blood and urine (compare Burns, A., 1916, i, 617). G. B.

Cell Penetration by Acids. IV. Penetration of Phosphoric Acid. W. J. Crozier (*J. Biol. Chem.*, 1918, **33**, 463—470. Compare A., 1916, i, 694).—With mantle tissue of *Chromodoris*, the coagulating action of phosphoric acid is so pronounced that a relatively high concentration must be employed before there is marked acceleration in the speed with which the quantity of acid sufficient to react with the indicator is forced to diffuse into the tissue. The actual speed of protoplasmic penetration by phosphoric acid is probably much greater than its apparent magnitude.

H. W. B.

Catalase Content of Ascaris suum, with a Suggestion as to its Rôle in Protecting Parasites against the Digestive Enzymes of their Hosts. Thomas Byrd Magath (*J. Biol. Chem.*, 1918, **33**, 395—400).—The relative amounts of catalase contained in two or more tissues are estimated by measuring the volumes of oxygen evolved when equal weights of the tissues are placed in contact with excessive quantities of hydrogen peroxide. The apparatus employed is similar to that used for the estimation of urea by the hypobromite method; hydrogen peroxide is placed in the bottle together with a crucible containing the weighed tissue. The bottle is connected with a measuring burette and levelling tube filled with water. After the crucible has been upset, the oxygen evolved is readily measured and corrected for normal temperature and pressure.

The whole worm yields 15 c.c. of oxygen per gram, the body

wall 13 c.c., the body fluid 7 c.c., and the visceral organs 26 c.c. per gram. Whilst these amounts are small as compared with those obtained from free living animals, it is pointed out that if the catalase in the respective reproductive organs be taken as the unit, then the body wall of *Ascaris* contains three times as much catalase as the leg muscles of the frog. It is probable, therefore, that there is more than enough catalase in the body wall of this worm for its metabolic and locomotory functions, and it is possible that the excess is used to liberate oxygen for protecting the parasite against the digestive enzymes of its host (see Burge, A., 1915, i, 614).

H. W. B.

Food Fishes. Analysis of Twenty Common Food Fishes with Especial Reference to a Seasonal Variation in Composition. ERNEST D. CLARK and LLOYD H. ALMY (*J. Biol. Chem.*, 1918, **33**, 483—498).—The authors have analysed the edible portions of various fishes at different periods of time. In the case of the shad, the spawning period is about two months, during which time the fish appear in the rivers in April and ascend to fresh-water, returning to the sea in June. The amount of fat in the edible portion of the fish diminishes from 14·4% before spawning to 2·95% afterwards. The shad, like the salmon, does not feed during the spawning migration, and doubtless some of the fat is consumed in the tissues to furnish the energy necessary for ascending the rivers, and the remainder is transferred to the roe and milt.

In most fishes, the fat content varies inversely as the water content, the proportion of fat-free solids remaining constant. The fish oils are fairly uniform, the constants being D_{25}^{25} 0·9220, n_D^{30} 1·4750, iodine number 110—130, and saponification number 180—190. The amounts of water-soluble nitrogen and coagulable nitrogen are also fairly constant for the same kind of fish taken at different times, whilst the amounts of these substances may be widely different for different species of fish. H. W. B.

The Biochemistry of Certain Conditions of Oedema. I. Blood and Serum. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **85**, 365—405).—The investigations refer to certain cases of "œdema disease" observed chiefly in prisoners of war. The chief results were the following: Diminution in blood, especially in the plasma of fatty acids and lipoid phosphorus; hypoglycæmia, increase in acetone substances, residual nitrogen, ammonia, cholesterol, and acid-soluble phosphorus; small increase in sodium chloride. Diminution of iron and potassium; moderate hydræmia, but, with the exception of lymphocytosis, no marked abnormality in the formal elements of the blood, and other characters. The author discusses the clinical bearings of the results. S. B. S.

The Part Played by an "Accessory Factor" in the Production of Experimental Rickets. EDWARD MELLANBY (*Proc. Physiol. Soc.*, 1918, xi—xii; *J. Physiol.*, **52**).—Two diets,

(1) milk, rice, oatmeal, and sodium chloride, (2) milk and bread, produce rickets in puppies in the course of three to four months if the milk is kept below 200 c.c. per day. Rickets was prevented by extracts of meat, malt, and yeast, by butter, margarine, and cod-liver oil, but not by protein of meat, casein, linseed oil, or 10 grams of yeast per day. Hence it would appear that rickets is due to the lack of an accessory factor in the diet. G. B.

Degradation of Aliphatic Acids in the Animal Body. EMIL LENK (*Münch. Med. Woch.*, 1917, **64**, 1460; from *Chem. Zentr.*, 1918, i, 121).—The author has shown that acetoacetic acid may be oxidised to acetic acid by heating with acetic acid and permanganate (A., 1917, ii, 399), and believes that a similar degradation of the acid by the attack of oxidising agents on the ethylene linking (of the enolic modification) may proceed in the body. Other facts indicate that acetic acid may be formed in the body as the result of reduction, so the degradation of fatty acids, which is so complete that only traces of the higher members are ever found in normal urine, may be due to both processes. J. C. W.

Elimination of Taurine administered to Man. CARL L. A. SCHMIDT, EDWARD VON ADELUNG, and THOMAS WATSON (*J. Biol. Chem.*, 1918, **33**, 501—503).—The administration of from 3 to 10 grams of taurine subcutaneously, intravenously, or by the mouth is followed by an increased elimination of neutral sulphur in the urine. From 59 to 86% of the taurine sulphur is thus recoverable from the urine. Large doses of taurine administered to rabbits or to human subjects do not appear to produce any toxic effects. H. W. B.

The Character of the Toxic Action of Suprarenine [Adrenaline]. OSCAR LOEW (*Biochem. Zeitsch.*, 1918, **85**, 295—306).—When in the form of its salts in a neutral solution, adrenaline has only a very slightly toxic action. The free base, however, and its first red oxidation product is extremely toxic, and this action can be readily demonstrated on the nucleus of *Spirogyra*. The author ascribes the toxicity to the lability of the hydrogen ions in the molecule, which is specially marked in alkaline solution. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Nitrogen Content of Bacterial Cells. I. Method. HAROLD C. BRADLEY, and M. STARR NICHOLS (*J. Biol. Chem.*, 1918, **33**, 525—529).—The bacterium is grown on a solid medium and the culture then transferred by a glass spatula to a tared

cover-slip and dried at 37° in a desiccator to constant weight. The nitrogen is subsequently estimated by Folin's micro-method.

Employing quantities of about 5 mg. of dry bacteria for analysis, *B. diphtheriae* are found to contain about 8·4, and *B. hoffmanni* 9·6 per cent. of nitrogen. H. W. B.

The Bacterial Metabolism of Sulphur. II. Formation of Hydrogen Sulphide from certain Sulphur Compounds by Yeast-like Fungi. FRED W. TANNER (*J. Amer. Chem. Soc.*, 1918, **40**, 663—669).—The growth of some thirty varieties of budding fungi, mainly yeast species, has been studied in culture media containing peptone, cystine, sodium thiosulphate, sulphate, and sulphite, potassium thiocyanate, thiocarbamide, sodium phenolsulphonate and taurocholate, or sulphur itself. All of them were found to produce hydrogen sulphide from cystine, but only eleven developed it from peptone; twenty-two varieties gave very positive results with the thiosulphate, and distinct lead paper reactions when grown with the sulphite, whilst ten reduced even the sulphate; about two-thirds produced hydrogen sulphide from free sulphur; sodium taurocholate was reduced by two varieties only, and the phenolsulphonate by *Mycoderma lactis* only, although growth was quite good on this substrate. *M. lactis* has the largest all-round reducing power. J. C. W.

Bactericidal Properties conferred on the Blood by Intravenous Injection of Diaminoacridine Sulphate. C. H. BROWNING and R. GALBRANSEN (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 136—144).—Attention is directed to the fact that certain acridine derivatives, unlike most other antiseptics, have a stronger bactericidal action in the presence than in the absence of serum, and, furthermore, that the toxic action increases progressively with time. Some experiments show that when diaminoacridine sulphate is injected into rabbits, their sera become bactericidal to *Staphylococcus aureus* and *B. coli*, even after heating at 56°. S. B. S.

Enzyme Formation. HANS EULER (*Biochem. Zeitsch.*, 1918, **85**, 406—417).—Attention is directed to the fact that the formation of a ferment (invertase) in developing yeast is not necessarily parallel with the rate of growth. A series of experiments was carried out with culture media containing, in addition to sucrose and the necessary inorganic salts, the following substances as sources of nitrogen: glycine, glycine + cystine, glycine + tyrosine, asparagine, alanine, and yeast water. There was no marked difference in the rate of growth with different amino-acids, but it was less than that in yeast water. In yeast water, the rate of formation of invertase was greater than in presence of pure amino-acids, but here again there was no marked difference in the action of the individual acids. S. B. S.

Volutin and its Chemical Composition. M. A. VAN HERWERDEN (*Folia Microbiologica. Nederl. Tydschr. voor Mikrobiologie*, 1917, **5**, pp. 12; from *Chem. Zentr.*, 1918, i, 216).—If

organisms like *Ustilago maydis*, *Torula monosa*, lactose yeast, or *Saccharomyces cerevisiae* are cultivated on media which are free from phosphates, they do not develop volutin, but this immediately appears in the cells if the cultures are transferred to a phosphate mixture. A nucleic acid derivative is also extracted from ordinary cultures when the isolation of volutin is aimed at, but the same procedure fails to remove nucleic acid compounds from a culture which contains no volutin. The conclusion is therefore drawn that volutin itself is a nucleic acid derivative. The living cell, even if volutin is absent, contains zymase, catalase, and nuclease, the latter being able to liberate phosphoric acid from nucleic acids. The stimulation of fermentation by volutin is therefore probably due to the steady production of small quantities of phosphoric acid from it.

J. C. W.

The Plasmotype-Volumetric Method and its Applicability to the Measurement of the Osmotic Value of Living Plant Cells. KARL HÖFLER (*Ber. Deut. bot. Ges.*, 1917, **35**, 706—726).—In the original experiments of de Vries, a comparison was made between the concentrations of the solutions of different substances which were just capable of producing perceptible plasmolysis in the immersed plant cells. When more concentrated external solutions are employed, plasmolysis takes place until the issuing water has reduced the volume of the cell sap to such an extent that the internal and external solutions are isotonic. By the use of suitable plant cells, it is possible to measure the volume of the protoplast when equilibrium has been reached by means of a measuring microscope, and from the relation between this volume and the volume of the cell, the osmotic concentration of the original cell sap may be calculated. The results obtained in a series of experiments in which the concentration of the external (sucrose) solution was varied show a close agreement. It seems possible that the method may be applied in the investigation of the deviations of the osmotic concentration of cells from the average or normal values.

H. M. D.

The Physiologically Active Constituents of certain Philippine Medicinal Plants. II. HARVEY C. BRILL and ALBERT H. WELLS (*Philippine J. Sci.*, 1917, **12**, [A], 167—198. Compare A., 1907, ii, 500).—A continuation of the examination of medicinal plants occurring in the Philippine Islands. A summary of previous knowledge and of native applications of the plants is given in each case.

Lophopetalum toxicum, Loher (N.O., *Celastraceae*), is a tree from the bark of which the natives obtain a juice with which to poison their weapons, care being taken by them not to leave the extract in contact with sour substances. A yield of 0·8% of a very toxic saponin, crystallising in clusters of needles, m. p. 183°, was obtained from the fresh bast fibre.

The bark of *Erythrophloeum densiflorum*, Merrill (*Leguminosae*),

contains tannins but no alkaloids, the substance erythrophleine found in *E. guineense* being absent from this species.

Quisqualis indica, Linn. (*Combretaceae*), gives fruits with yellow kernels which have been a popular anthelmintic and laxative in the East for some centuries. The seeds contain a yellow oil, possessing purgative but not anthelmintic properties, a sugar, 3·87% of potassium sulphate, and a gum which shows many alkaloidal reactions.

Tylophora brevipes, F.-Vill. (*Asclepidaceae*), is valued by the Filipinos as an emetic and expectorant, a decoction of the roots being used. The plant is closely related to *T. asthmatica*, well known in India for its resemblance in properties to ipecacuanha, and it contains the same alkaloid, tylophorine (Hooper, A., 1891, 1267).

Toddalia asiatica, Kurz (*Rutaceae*), has been widely known for centuries on account of the febrifugal and anti-diarrhœal properties of its roots, being mentioned in old pharmacopœias as "*Radix indica lopeziana*," or *tinct. toddalia*, especially in India. Its active principle is berberine.

Lunasia amara, Blanco (*Rutaceae*), the native name for which signifies "bitterness itself," provides a close-grained wood which is so hard that the Negritos often use it for the tips of their arrows, but not to poison the weapons, as is wrongly supposed. The juice of the seeds is used against the bite of poisonous animals, and the bark and seeds are held to be useful in gastralgia. The bark and leaves contain about 0·6% of intensely bitter alkaloidal substances of moderate physiological activity, wholly or chiefly consisting of lunasine, already reported by Boorsma. Prior to Boorsma's work in 1900, it appears that all accounts of *Lunasia* were founded on specimens sent to European museums, which were really *Lophopetalum toxicum*.

Rourea erecta, Merrill (*Connaraceae*), is a vine, the roots and berries of which are used by native quack doctors for a variety of ailments. The berries, even old, dry specimens, contain an active principle which is very toxic to carnivora but not to herbivora.

Hymenodictyon excelsum (*Rubiaceae*) of the Philippines contains no alkaloid, but differs from Indian varieties in that the active febrifuge is not æsculin, but β-methylæsculetin (compare Gibson and Simonsen, this vol., i, 151). The product isolated had m. p. 203°, and gave an *acetyl* compound, rhombic prisms and plates, m. p. 177°, and agreed with Schmidt's compound from *Gelsemium sempervivens* (A., 1899, i, 72). J. C. W.

Organic Chemistry.

The Oxidation Products of Paraffin. MAXIMILIAN BERGMANN (*Zeitsch. angew. Chem.*, 1918, **31**, 69—70).—White, refined paraffin wax of Galician origin, m. p. 52°, was oxidised by blowing a fairly rapid current of air through it at 130—135° for fifteen to eighteen days. The soft brown product of the oxidation had an acid value of 132 and gave strongly frothing soap solutions with alkali hydroxides. On distilling the crude mass, decomposition set in at about 300°, with formation of formic, acetic, and *n*-butyric acids. The separation of the fatty acids from the neutral substances was therefore effected by formiug the barium soaps and extracting the dried precipitate with ether. The isolated fatty acids had an acid value of 200 and were fractionated by distillation under 100 mm. pressure; about one-half distilled betwen 230° and 270° and one-third between 270° and 310°. The latter fraction showed an iodine value of 4; it was converted into the lithium soap, which was dried and extracted with ether and light petroleum, to separate the last traces of unsaponifiable matter. The liberated fatty acid was converted into the ethyl ester, m. p. 55°, after recrystallisation from alcohol. The purified acid had m. p. 80·1°. It was thus characterised as *lignoceric acid*, and proved to be identical with the lignoceric acid prepared from earth-nut oil. The fraction boiling between 230° and 270° had an iodine value of 5; by extraction of its lithium soap, a neutral substance was extracted crystallising from methyl alcohol in leaflets, m. p. 48°. The liberated fatty acids were separated by crystallisation from acetic acid into two substances: one crystallising in shining needles, m. p. 53·7°, acid value 299·4, corresponding with the formula $C_{11}H_{22}O_2$, which gave strongly frothing soap solutions with alkali hydroxides; and the other, separated from the mother liquors by precipitation as the lithium soap, which had m. p. 210—212°, having a composition corresponding with $C_{16}H_{32}O_2$, m. p. 38·4°, and acid value 217·05. The latter acid might be an *iso*palmitic acid. J. F. B.

Solubility of Hydrocarbons (Paraffin, Aromatic, Naphthene and Olefine) in Liquid Sulphur Dioxide. R. J. MOORE, J. C. MORELL, and G. EGLOFF (*Met. and Chem. Eng.*, 1918, **18**, 396—402).—The solubility of individual hydrocarbons, of binary mixtures, and of a ternary mixture, of paraffins, aromatic hydrocarbons, and naphthenes has been studied. Solubilities were determined by bringing the liquid sulphur dioxide and the hydrocarbons together in a burette immersed in a freezing mixture of ice, salt, and calcium chloride at temperatures down to −18°. Benzene, toluene, xylene, mesitylene, and olefines were miscible with the solvent in all proportions. Paraffins up to decane were practically insoluble. Naphthenes showed a solubility limited

at $-18°$, which was more pronounced at $-4·5°$. There is evidence of the formation of a molecular compound with the solvent. The separation of the mixed hydrocarbons of different types by liquid sulphur dioxide is limited by the partition of the hydrocarbons between the two phases, but by attention to the relative proportions, *some approximation to a quantitative separation is possible*, generally where the constituent to be extracted is in small proportion. Aromatic hydrocarbons and olefines, together or separate, can be separated from paraffins and naphthenes. Naphthenes can be separated from paraffins. Over methods of sulphonation and nitration, this method has the advantage of permitting recovery of both hydrocarbon and solvent and also of avoiding the production of undesirable by-products . H. J. H.

Action of Concentrated Sulphuric Acid on Olefines, with Particular Reference to the Refining of Petroleum Distillates. BENJAMIN T. BROOKS and IRWIN HUMPHREY (*J. Amer Chem. Soc.*, 1918, **40**, 822—856).—The data at present available as to the behaviour of various olefines with sulphuric acid are scanty and somewhat conflicting, and as a preliminary to an investigation of the action of sulphuric acid on olefines as applied in the refinery of petroleum distillates, the authors have examined the effect of sulphuric acid on synthetic unsaturated hydrocarbons of definite purity and known constitution.

The chief results of the action of sulphuric acid on olefines are polymerisation and the formation of secondary and tertiary alcohols and of alkyl hydrogen and dialkyl sulphates. Contrary to the general assumption in the petroleum industry, no mono-olefine hydrocarbon was found to yield a "tar" when treated with the acid at 15°. In the aliphatic series, the tendency to form alkyl sulphates and alcohols decreases with increasing molecular weight above the amylenes and hexenes, at which a maximum is observed (compare Michael and Brunel, A., 1909, i, 197; 1912, i, 821). The introduction of strongly electronegative groups into ethylene causes a decrease in the reactivity towards sulphuric acid, as is demonstrated by the relative inertness of fumaric and cinnamic acids and of dichloroethylene towards the acid, whilst, inversely, $\beta\gamma$-dimethyl-Δ^{β}-butylene, in which each of the hydrogen atoms is replaced by the electro-positive methyl radicle, is more reactive than the isomeric α-hexene; a similar consideration also explains the greater reactivity of amylene, butylene, and propylene as compared with ethylene. This point of view, however, fails to explain the relative stability of the olefines of still higher molecular weight, nor does it appear to throw much light on the difference between the behaviour of γ-ethyl-Δ^{β}-pentene, which yields 72% of the alcohol and 12% of polymerides and of the structurally similar β-methyl-Δ^{β}-undecene, which gives 97% polymerides and a trace of alcohol, or on the fact that vinylacetic acid yields crotonic acid, whereas the isomeric α-methylacrylic acid gives a polymerisation product; styrene, cinnamyl alcohol, eugenol, *iso*eugenol, and safrole also

undergo vigorous polymerisation to hard, resinous substances. With increasing molecular weight, the tendency towards polymerisation develops, and duodecene is found to undergo almost quantitative conversion into a dipolymeride; the polymerides generally are open-chain hydrocarbons still containing at least one double bond, and are naturally much more stable than the parent olefines towards sulphuric acid; the result of this is that when petroleum is refined with sulphuric acid, the viscous polymerides are not found in the used acid, but remain to a large extent in the layer of refined oil. The common assumption that the more viscous petroleum oils, for example, of the lubricating oil type, consist exclusively of naphthenes and polynaphthenes is therefore not above suspicion, and the presence of a considerable percentage of polymerised olefines is probable, not only from the fact that the oils have been treated with sulphuric acid, but from the definite iodine value of such oils.

When the simpler alkylenes are dissolved in cold 85% sulphuric acid at below 15°, clear amber-coloured solutions are obtained which on treatment with ice give an immediate oily precipitate consisting mainly of the corresponding alcohol, whilst the aqueous acid solution, containing a considerable proportion of the original hydrocarbon as the alkyl hydrogen sulphate, fails to yield any appreciable further deposit of oil even during several days; the alkyl hydrogen sulphates, therefore, are not readily hydrolysed under such conditions; from these results and the fact that pure sulphuric acid alone does not convert hexenes into the alcohols, it is probable that the formation of alcohols by the action of diluted sulphuric acid on alkylenes may be independent of any intermediate occurrence of sulphuric esters of the known type and may be attributed to the intermediate formation of an easily hydrolysable orthosulphate analogous to sulphuric acid monohydrate, H_4SO_5, or of an easily hydratable additive compound of the olefine with sulphuric acid corresponding with the zinc chloride or aluminium chloride additive compounds (compare Gangloff and Henderson, A., 1916, i, 593; 1917, i, 533).

In the course of the investigation, the following olefinic hydrocarbons were examined in a high degree of purity: *β*-methyl-Δ^{α}-butylene, b. p. 33—35°; *β*-methyl-Δ^{α}-pentene, b. p. 64—66°; Δ^{α}-*n*-hexene, b. p. 60·5—61·5° (earlier descriptions are inaccurate), the constitution of which is demonstrated by its conversion through the chlorohydrin into the corresponding glycol; *ε*-methyl-Δ^{α}-hexene (*iso*heptene), $CHMe_2·CH_2·CH_2·CH:CH_2$, b. p. 85—86°, D_{15}^{15} 0·7160; Δ^{γ}-*n*-heptene, b. p. 93—95°, D_{20}^{20} 0·7020, which combines with benzenesulphonic acid at the ordinary temperature, yielding an undistillable heptyl benzenesulphonate, D_{20}^{20} 0·979; *γ*-ethyl-Δ^{β}-pentene, b. p. 97—98°; *βγ*-dimethyl-Δ^{β}-butene (tetramethylethylene), b. p. 73—74°, D_{20}^{20} 0·7075; Δ^{α}-octene, b. p. 122—124°, D 0·7240 (dipolymeride, b. p. 195—230°), although it is not certain that this may not in reality be the Δ^{β}-isomeride; *ζ-methyl-Δ^{α}-heptene* (*isooctene*), $CHMe_2·CH_2·CH_2·CH_2·CH:CH_2$, b. p.

111—112°, D_4^{20} 0·7125, n_D^{20} 1·3986 (*dipolymeride*, b. p. 112—114°/16 mm., D 0·798); *β-methyl-Δ^β-undecene*, $CMe_2{:}CH{\cdot}C_8H_{17}$, b. p. 210—211·5°/752 mm., D_4^{20} 0·7590, n_D^{20} 1·4270. For the synthetic production of Δ^a-ethylenic hydrocarbons, the interaction of allyl bromide and a magnesium alkyl bromide was found convenient; the formation of unsaturated hydrocarbons by the action of heat on the higher alcohols is found to be greatly facilitated by the addition of a little iodine. In the preparation of ζ-methyl-Δ^a-heptene by the former method, using magnesium *iso*amyl bromide and allyl bromide, a *decane*, b. p. 156·5—157·5°, n_D^{20} 1·4006, D_{20}^{20} 0·7270, probably of the constitution $C_2H_4(CH_2{\cdot}CHMe_2)_2$, was obtained as a by-product. D. F. T.

Preparation of Glycols. Chemical Development Co. (U.S. Pat. 1259757).—A mixture of olefine dichlorides prepared from oil-gas is converted into the corresponding glycols (ethylene, propylene, and butylene glycols) by heating with water and calcium carbonate under pressure. A. S.

Preparation of Glycols and Glycol Derivatives. Chemical Development Co. (U.S. Pat. 1259758).—A mixture of olefine dihaloids is heated under pressure with the calcium salt of a weak acid, for example, calcium acetate. (See also preceding abstract.) A. S.

Lecithin. II. Preparation of Pure Lecithin; Composition and Stability of Lecithin-Cadmium Chloride. P. A. Levene and C. J. West (*J. Biol. Chem.*, 1918, **34**, 175—186. Compare this vol., i, 98).—Pure lecithin may be obtained from egg yolk by extracting with acetone and alcohol, and then redissolving the concentrated extract several times in dry acetone, which effects a separation from lipoids insoluble in acetone. The oil is then extracted with a large volume of hot alcohol, the alcoholic extract cooled to 0°, the solution decanted from the egg-fat, concentrated, and the lipoid mixture precipitated with cadmium chloride. The lecithin-cadmium chloride is recrystallised from a mixture of ethyl acetate and 80% alcohol until free from amino-nitrogen (kephalin), and is then decomposed by ammonium carbonate according to Bergell's method (A., 1900, i, 621). The resulting lecithin does not contain any amino-nitrogen. H. W. B.

Preparation of Acetic Acid from Acetaldehyde. H. Dreyfus (Brit. Pat. 108459. Compare this vol., i, 251).—The oxidation of acetaldehyde to acetic acid by means of air or oxygen, either in presence or absence of contact substances, is most complete if effected at 150—250°, preferably 150—200°. Copper (clippings, gauze, powder) is a more efficient catalyst than platinum. Chromium compounds are also very efficient, and other suitable catalysts are copper oxide, iron, uranium oxide, vanadium oxide, and cerium oxide. A. S.

Preparation of Acetic Anhydride and Polymerised or Non-polymerised Acetaldehyde. Société Chimique des Usines du Rhône (Brit. Pat. 110906).—Ethylidene diacetate is decomposed almost quantitatively into acetic anhydride and paraldehyde by heating it in a vacuum with an acid or acid salt as catalyst, for example, with 2% of sulphuric acid (D 1·84) at 70—80°/100 mm. A. S.

The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol. Mary Evelyn Laing (T., 1918, **113**, 435—444).—Measurements have been made of the changes in the boiling point of ethyl alcohol which are produced by the addition of gradually increasing quantities of potassium oleate. The molecular weight calculated from the results is independent of the concentration and slightly less than that corresponding with the formula. In moist alcohol similar results were obtained.

From the measured values of the electrical conductivity at 40° and 60°, it is inferred that the ionisation increases from about 3% in 1*N*- to about 30% in 0·03*N*-solution.

The conductivity of solutions of oleic acid in ethyl alcohol has also been measured at 60° over a wide range of concentration. The degree of ionisation is very small, and the results afford evidence that the ionisation varies with dilution in accordance with the requirements of the law of mass action.

The conductivity of potassium oleate in alcohol is diminished by the addition of oleic acid. This suggests the formation of a complex compound, and evidence in support of this hypothesis is afforded by boiling point observations on solutions containing mixtures of the salt and acid.

The observations on potassium oleate agree with those previously made by Krafft on the salts of other fatty acids and show that these substances behave as normal electrolytes in alcohol, although in aqueous solution they afford examples of colloidal electrolytes.

H. M. D.

Preparation of a Crystalline Ester of the Di-iodide of Ricinstearolic Acid. J. D. Riedel (D.R.-P., 303052, 1914; from *Chem. Zentr.*, 1918, i, 498).—Ethyl ricinstearolate di-iodide, colourless needles, m. p. 31°, can be obtained by esterifying the di-iodide of ricinstearolic acid or by the addition of iodine to ethyl ricinstearolate. D. F. T.

Ethyl Thioacetoacetate [Ethyl Acetoacetate Sulphide], Ethyl α-Chloroacetoacetate, and a New Formation of Oxalic Acid. Fr. von Konek-Norwall (*Ber.*, 1918, **51**, 391—398).—When antipyrine is treated with sulphur chlorides, it yields a mono- and di-sulphide (A., 1911, i, 505), but the parent ethyl acetoacetate only forms a monosulphide, $S(CHAc \cdot CO_2Et)_2$ (A., 1885, 1200). With the hope of obtaining a disulphide, some pure ethyl α-chloroacetoacetate was purchased about six years ago to

be treated with sulphur, but it was recently found that the specimen had gradually deposited crystals of oxalic acid dihydrate.

J. C. W.

Photochemical Reactions in Aqueous Solution. II. ALFRED BENRATH (*J. pr. Chem.*, 1917, [ii], **96**, 190—201. Compare A., 1912, ii, 881; 1911, ii, 681).—When mixed with iron alum in aqueous solution in a sealed glass tube exposed to sunlight, tartaric acid undergoes photochemical oxidation with formation of dihydroxytartaric acid, which is not isolable, but rapidly decomposes in part into glyoxalcarboxylic acid, $CHO\cdot CO\cdot CO_2H$, and carbon dioxide (compare Ciamician and Silber, A., 1913, ii, 545; Seekamp, A., 1894, i, 323); the formation of this acid is proved by its isolation as its di-phenylhydrazone and by the relative proportion of the reagents which participate in the change. Part of the dihydroxytartaric acid, however, undergoes further oxidation to carbon dioxide, probably by way of mesoxalic acid, and carbon dioxide is also formed as the final product in the further oxidation of the glyoxalcarboxylic acid, probably through tartronic acid and mesoxalic acid; small quantities of glyoxal, glyoxylic acid, and formaldehyde can also be detected, but these are regarded as by-products, the first being produced by the partial elimination of carbon dioxide from glyoxalcarboxylic acid, whilst the last two form minor successive oxidation products of mesoxalic acid. The correctness of these views is confirmed by photochemical experiments with the postulated intermediate products.

Citric acid in aqueous solution, with the addition of iron alum and a little sulphuric acid, becomes oxidised in sunlight during the course of a few days with formation of carbon dioxide, acetone, and a little formaldehyde. In a similar oxidation of glycollic acid, formaldehyde and glyoxylic acid can be detected, whilst malic acid is relatively resistant, and the only identified products were acetaldehyde and formaldehyde.

When a mixture of formic acid with ethyl alcohol, or acetic acid with methyl alcohol, in a sealed tube is exposed to light for twelve months, the resulting liquid can be shown to contain the corresponding ester, together with formaldehyde and acetaldehyde in addition to unchanged ingredients, whilst with acetic acid and ethyl alcohol only ethyl acetate and acetaldehyde are formed; the conclusion is drawn that the resulting ester undergoes partial decomposition into the two aldehydes. In a similar manner, a mixture of formic and malic acids produces carbon dioxide, formaldehyde, and acetaldehyde, and the same substances are formed in the interaction of oxalic acid and acetone; a mixture of formic acid and citric acid yields carbon dioxide, formaldehyde, and acetone, and a mixture of formic acid and acetone gives rise to formaldehyde.

D. F. T.

Formaldehyde in Air. D. G. J. BOLTEN (*Pharm. Weekblad*, 1918, **55**, 60—61).—The evolution of formaldehyde vapour from formalin for disinfecting purposes can be brought about by the action of quicklime. The process has the advantage that there

is no oxidation of the formaldehyde. In the permanganate method 2% of the formaldehyde is lost through oxidation. A. J. W.

Preparation of Dialdehydesulphoxylic Acids. ARTHUR BINZ (D.R.-P., 303478, 1916; from *Chem. Zentr.*, 1918, i, 498).—*Diformaldehydesulphoxylic acid*, $S(O{\cdot}CH_2{\cdot}OH)_2$, can be obtainec from a formaldehydesulphoxylate, formaldehyde solution, and alco holic hydrogen chloride; similarly, *dibenzaldehydesulphoxylic aci* is obtainable from benzaldehydesulphoxylate. The analogous *form aldehydebenzaldehydesulphoxylic acid*, $OH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}O{\cdot}CHPh{\cdot}OH$ reacts with p-*toluidine*, yielding the *substance*

$$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}O{\cdot}CHPh{\cdot}OH.$$

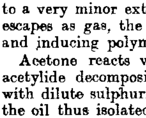
D. F. T.

Action of Sodium Acetylide on Aldehydes and Ketones K. HESS and H. MUNDERLOH (*Ber.*, 1918, **51**, 377—384).—Primary, secondary, and tertiary alcohols of the acetylene serie have been prepared by the action of sodium phenylacetylide CPh:CNa, on formaldehyde, other aldehydes and ketones, respe tively (*compare Nef, 1899, and Moureu, 1901—1902*). The be haviour of unsubstituted sodium acetylide, CH:CNa, has there fore been examined. This is found to react in the above manne to a very minor extent. Generally speaking, most of the acetylen escapes as gas, the sodium uniting with the carbonylic compoun and inducing polymerisation and intermolecular condensations.

Acetone reacts vigorously, even at $-15°$, about 64% of th acetylide decomposing into gas. After decomposing the produc with dilute sulphuric acid, extracting with ether, and fractionatin the oil thus isolated, the following compounds were obtained: (1 *γ-Methylbutinen-γ-ol*, $OH{\cdot}CMe_2{\cdot}C{:}CH$, a volatile, mobile, pungent smelling oil, b. p. 102—103°/745 mm., 25°/12 mm., yield 2·8% this gives a white precipitate with mercuric chloride which yield trimethylketol, identified by its semicarbazone (Schmidt an Austin, A., 1902, i, 2), on boiling with hydrochloric acid. (II. Mesityl oxide, sufficient in quantity to identify as its semicarbazon (III.) Diacetone alcohol, b. p. 67—68°/19 mm., yield about 1·3% (IV.) *iso*Phorone, b. p. 86—87°/11 mm., yield 36·9%; this ha been identified by its semicarbazone and also reduced by sodiu amalgam to the *pinacone*,

$$CH_2{<}{\begin{matrix}CMe_2{\cdot}CH_2\\CMe{=}CH\end{matrix}}{>}C{\begin{matrix}OH\\ \end{matrix}}\!-\!\!-\!\!-\!{\begin{matrix}OH\\ \end{matrix}}C{<}{\begin{matrix}CH_2{\cdot}CMe_2\\CH{=}CMe\end{matrix}}{>}CH_2,$$

m. p. 162°. (V.) "*iso*Phorone-acetylene" (annexed formula), viscous, pungent oil, b. p. 115—116°/12 mm yield 2·2%.



Reaction with acetaldehyde is still mor vigorous. The only recognisable product i a minute quantity of *butinen-γ-ol*,

$$OH{\cdot}CHMe{\cdot}C{:}CH,$$

which is a limpid, lachrymatory oil, b. p 105—106°/742 mm. Benzaldehyde gives a the chief product benzyl benzoate.

Notes on the preparation of sodium acetylide are given. J. C. W.

The Influence of Certain Substances on Starch Solutions, and the Action of Amylase of the Saliva. J. Temminek Groll (*Arch. néerland. physiol.*, 1918, **2**, 319—336).—Reversible transformations of starch into an erythroamylose, giving a red or violet colour with iodine-potassium iodide solution, take place when starch solutions are treated with methyl, ethyl, or octyl alcohol, ethyl ether, and chloroform in various concentrations. If sodium cholate or saponin is added in addition to these substances, the transformation into erythroamylose becomes irreversible. This action of cholate and saponin is ascribed to a surface-tension effect. The salivary amylase, under the influence of cholate and saponin, acts on starch solutions, producing reducing substances which colour the iodine solution red or brown. After some minutes, however, the starchy substance is reconstituted, the reducing substances disappear, and the solution gives a blue colour with iodine. After a further long period, the starchy substance disappears, and products are produced which do not colour iodine. It is suggested that it is possible, by simply lowering surface tension, to obtain catalytic decomposition of a colloidal substrate (soluble starch).

S. B. S.

Wood Pulp. Carl G. Schwalbe (*Zeitsch. angew. Chem.*, 1918, **31**, 50—56; 57—60).—A description of the different classes of wood pulp and of its chemical properties. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

Two Forms of Glycine. K. George Falk and Kanematsu Sugiura (*J. Biol. Chem.*, 1918, **34**, 29—36. Compare Fischer, A., 1905, i, 863).—Glycine crystallises from water in plates and from dilute alcohol in needles. After drying at 100°, the plate form begins to decompose on heating at 212°, whilst the needle form remains unchanged until a temperature of 220° to 230° is reached. There are also differences in the behaviour of the two forms towards nitrous acid and towards bromine; in one experiment, each molecule of the needle form absorbed 2 atoms of bromine, whilst the plate form absorbed 1 atom. Similar experiments with the corresponding two forms of alanine showed similar although less marked differences. Possible structural formulæ are suggested to account for the observed differences between the two forms of glycine and alanine respectively.

H. W. B.

Preparation of Formamide. Albert Brann (*J. Amer. Chem. Soc.*, 1918, **40**, 793—796).—Formamide purified by fractional distillation has m. p. 2·25° (English and Turner, Trans., 1914, **105**, 1656, give 2·0—2·2°). [See also *J. Soc. Chem. Ind.*, July.]

D. F. T.

Rotatory Powers of the Amides of Active α-Hydroxy-acids. C. S. Hudson (*J. Amer. Chem. Soc.*, 1918, **40**, 813—817).—The sign of the optical activity of the amides of *d*-gluconic acid, *d*-galactonic acid, *l*-mannonic acid, *d*-gulonic acid, *l*-arabonic acid, *l*-ribonic acid, and *d*-xylonic acid (Weerman, A., 1915, i, 387;

1917, i, 546), as also of the amides of *d*-α-glucoheptonic acid and of *l*-rhamnonic acid in aqueous solution, is in agreement with the general rule that the dextrorotatory amides have the α-hydroxyl group below the asymmetric α-carbon atom, whilst with the lævorotatory amides it is above, the constitutions being represented by ordinary plane formulæ placed horizontally with the amide group to the right (compare Levene, A., 1916, ii, 3; Levene and Meyer, A., 1916, ii, 545; 1917, i, 631; Hudson, A., 1910, i, 220; 1917, i, 318). This result is in accord with the structure of *d*-tartaric acid as decided by Fischer (A., 1896, i, 525) and with the direction of the optical activity of tartramic acid (Weerman, *loc. cit.*) and of the amides of tartaric acid (Frankland and Slator, T., 1903, **83**, 1354; Frankland and Twiss, T., 1906, **89**, 1853). The optical activities of the amide of *l*-malic acid (Walden, A., 1896, i, 139) and of the amide of *d*-glyceric acid (Frankland and Wharton, T., 1901, **79**, 266) are also found to obey this rule, and the agreement serves to confirm the structures attributed to these acids (Freudenberg, A., 1914, i, 924). The amide derived from amygdalin mandelic acid has a lævorotation, and on this evidence the α-hydroxyl group in this mandelic acid is believed to occupy a position above the asymmetric atom when the structure is formulated in the manner described. D. F. T.

Hydrazides and Azides of Organic Acids. XXXIII. The Action of Hydrazine and Nitrous Acid on Di- and Tri-glycollamic Esters. THEODOR CURTIUS and OTTO HOFMANN (*J. pr. Chem.*, 1917, [ii], **96**, 202—235).—Iminodiacetic acid (diglycollamic acid) can be obtained conveniently by heating chloroacetic acid with the additive compound of zinc chloride and ammonia, esterifying the resulting mixture of acids by heating with alcoholic hydrogen chloride and then separating the ethyl esters of aminoacetic acid, iminodiacetic acid, and nitrilotriacetic acid by distillation under reduced pressnre; another very convenient process is based on that of Jongkees (A., 1908, i, 959) for the preparation of iminodiacetonitrile, which by treatment with alcoholic hydrogen chloride can be converted directly into ethyl iminodiacetate (compare Dubsky and Gränacher, this vol., i, 188); if iminodiacetonitrile is suspended in ether and submitted to the action of nitrous fumes, nitrosoiminodiacetonitrile is obtained, m. p. 43° (Bailey and Snyder, A., 1915, i, 389, give m. p. 38°).

Ethyl iminodiacetate, $D^{15 \cdot 5}$ 1·0851, b. p. 133°/11 mm., reacts with hydrazine hydrate at the ordinary temperature, yielding *iminodiacetic hydrazide*, $NH(CH_2\cdot CO\cdot NH\cdot NH_2)_2$, leaflets or tablets, m. p. 133°, which forms a *trihydrochloride*, a *triacetyl* derivative, m. p. 204—205° (decomp.), and slowly reacts with ketones and aldehydes, giving *condensation products*; acetone, salicylaldehyde, and benzaldehyde respectively, giving rise to the *compounds*

$$NH(CH_2\cdot CO\cdot NH\cdot N:CMe_2)_2,$$

small rods, m. p. 176°; $NH(CH_2\cdot CO\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH)_2$, small rods, m. p. 201—202° (with decomp.); and

$$NH(CH_2\cdot CO\cdot NH\cdot N:CHPh)_2,$$

small rods, m. p. 201—202° (decomp.). If the condensation is allowed to proceed in the presence of mineral acid, the products are the corresponding salts of these substances, and always contain water of crystallisation, thus

$$2NH(CH_2\cdot CO\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH)_2,H_2SO_4,H_2O,$$

pale yellow solid, m. p. 190° (decomp.);

$$2NH(CH_2\cdot CO\cdot NH\cdot N:CHPh)_2,H_2SO_4,6H_2O,$$

m. p. 173—175°; $NH(CH_2\cdot CO\cdot NH\cdot N:CHPh)_2,HCl,2H_2O$, needles, m. p. 249—250°; $NH(CH_2\cdot CO\cdot NH\cdot N:CHPh)_2,HNO_3,2H_2O$, m. p. 202—203°; $NH(CH_2\cdot CO\cdot NH\cdot N:CHPh)_2,HNO_2,2H_2O$, m. p. indistinct near 135°; it was not found possible to convert the last, by dehydration, into a nitroso-compound.

On treatment with nitrous gases, ethyl iminodiglycollate is converted into *ethyl nitrosoiminodiacetate*, $NO\cdot N(CH_2\cdot CO_2Et)_2$, a viscous, yellow oil, b. p. 175°/14 mm., which is also obtainable from ethyl iminodiacetate hydrochloride and sodium nitrite in the presence of water, and from nitrosoiminodiacetonitrile by the action of alcohol and hydrogen chloride. Ethyl nitrosoiminodiacetate reacts with alcoholic ammonia solution, giving nitrosoiminodiacetamide, $NO\cdot N(CH_2\cdot CO\cdot NH_2)_2$, pale yellow tablets, m. p. 153°, and forms a dihydrazide (Curtius, Darapsky, and Müller, A., 1908, i, 145), which is convertible into a *diacetyl* derivative, m. p. 213—214° (decomp.), and readily condenses with acetone, producing a *substance*, $NO\cdot N(CH_2\cdot CO\cdot NH\cdot N:CMe_2)_2$, needles, m. p. 232° (decomp.). When treated in aqueous solution with sodium nitrite and the calculated quantity of hydrochloric acid, the nitrosohydrazide undergoes conversion into nitrosoiminodiacetic azide,

$$NO\cdot N(CH_2\cdot CO\cdot N_3)_2,$$

a yellow oil which reacts with hydrazine hydrate, re-forming the hydrazide, and on treatment with aniline gives *nitrosoiminodiacetanilide*, $NO\cdot N(CH_2\cdot CO\cdot NHPh)_2$, colourless needles, m. p. 224—225°. Boiling alcohol decomposes the azide in the normal manner, with formation of a *urethane* compound,

$$NO\cdot N(CH_2\cdot NH\cdot CO_2Et)_2,$$

colourless crystals, m. p. 70°, which reacts readily with cold hydrochloric acid, giving an effervescence of carbon dioxide and producing anhydroformaldehyde urethane, $C_8H_{14}O_4N_2$ (Conrad and Hock, A., 1903, i, 607), but can be completely hydrolysed to ammonia, formaldehyde, carbon dioxide, and alcohol by dilute hydrochloric acid in a sealed tube or by barium hydroxide solution; hot water causes a slow decomposition of the azide into nitrogen, carbon dioxide, a very soluble, vitreous *carbamide*, $NO\cdot N<\begin{matrix}CH_2\cdot NH\\CH_2\cdot NH\end{matrix}>CO$, and a trace of azoimide. If iminodiacetic hydrazide trihydrochloride is treated in the presence of a little water with sodium nitrite, liberation of nitrogen occurs, together with the formation of *iminodiacetic azide nitrite*,

$$(N_3\cdot CO\cdot CH_2)_2NH,HNO_2,$$

colourless needles, accompanied by the yellow nitroso-azide already mentioned; like the latter, the nitrite readily reacts with aniline, giving the nitrosoanilide.

Ethyl nitrilotriacetate (ethyl triglycollamate), prepared from the reaction product of chloroacetic acid and the additive compound of zinc chloride and ammonia or from nitrilotriacetonitrile, reacts only slowly with hydrazine hydrate, the resulting hygroscopic, vitreous *trihydrazide*, $N(CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2)_3$ (*tetrahydrochloride*), being converted by acetone and benzaldehyde into *condensation* products, $N(CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMe_2)_3$, small, colourless rods, m. p. 205° (decomp.), and $N(CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh)_3$, an amorphous powder, m. p. 206° (decomp.), respectively; the former can be converted into the latter by treatment with benzaldehyde. The addition of sodium nitrite to an aqueous solution of the nitrilotriacetic hydrazide hydrochloride causes immediate effervescence and formation of explosive leaflets of *nitrilotriacetic azide*,

$$N(CH_2{\cdot}CO{\cdot}N_3)_3,$$

together with a sparingly soluble substance, probably a hydraziazide. D. F. T.

Preparation of Trialkylethanolarsonium Hydroxides and their Salts. Chemische Werke Grenzach (D.R.-P., 303032, 1916; from *Chem. Zentr.*, 1918, i, 498).—By hydrolysis of halogenethyltrialkylarsonium haloids with water at higher temperatures, it is possible to produce arsonium compounds analogous to choline, and having valuable therapeutic properties. Trimethylarsine and ethylene bromide react at 100—105°, yielding *trimethyl-β-bromoethylarsonium bromide*, prismatic tablets, m. p. 239° (corresponding *picrate*, m. p. 189°), which is converted by water at 180° into *trimethylethanolarsonium bromide*, C_5H_4OBrAs, deliquescent prisms, m. p. 219°. *Triethyl-β-bromoethylarsonium bromide*, m. p. 225°, obtained from triethylarsine and ethylene bromide, on treatment with water at 180°, yields *triethylethanolarsonium bromide*, needles. D. F. T.

Preparation of Benzenesulphonic Acid. J. W. Aylsworth (U.S. Pat. 1260852).—Excess of benzene is heated with sulphuric acid in a closed vessel, at a temperature increasing progressively during several hours from 70° to 120°. The mass is then cooled below 70°, and, while stirring, a quantity of sulphur trioxide sufficient to combine with the water present is added, and the whole is again heated as before, the series of operations being repeated as many times as is necessary. A. S.

Preparation of *p*-Cymenesulphonic Acid. Rheinische Campher-Fabrik (D.R.-P., 303095, 1916; from *Chem. Zentr.*, 1918, i, 498).—2-Bromo-*p*-cymene-3-sulphonic acid can be conveniently reduced by heating with ordinary or activated zinc and sodium hydroxide solution. D. F. T.

Spinacene and some of its Derivatives. A. Chaston Chapman (T., 1918, **113**, 458—466. Compare *ibid.*, 1917, **111**, 56).—The author now assigns to spinacene the formula $C_{29}H_{48}$. It has b. p. 260° (corr.)/9 mm., D_{15}^{15} 0·8610, n^{20} 1·4956, iodine value

(Wij's method) 367·9. The hexahydrochloride has m. p. 126°, and when heated at 190°, under reduced pressure, loses its hydrogen chloride, and gives a *hydrocarbon* differing from spinacene in being less unsaturated. Dry hydrogen bromide, when passed into a cooled solution of spinacene in dry ether, gives a *hexahydrobromide*, $C_{29}H_{48},6HBr$, m. p. 132°. When warmed with dilute nitric acid (1 : 1), spinacene gives at least two products. When distilled over sodium at a pressure of 45 mm., spinacene is decomposed somewhat, four fractions being obtained: (1) b. p. 84—88°/45 mm.; (2) b. p. 155—175°/45 mm.; (3) b. p. 220—275°/45 mm.; (4) b. p. 295—298°/45 mm., and a colourless, viscous residue. Fraction (1), when purified by steam distillation, had b. p. 60°/20 mm., and was apparently a *cyclo*dihydroterpene, which may prove to be identical with *cyclo*dihydromyrcene or with *cyclo*linaloolene. W. G.

A New Dehydrogenation Method. Synthesis of Decacyclene, Fluorocyclene, and Chlorene, a Green Hydrocarbon. K. Dziewonski and S. Suknarowski (*Ber.*, 1918, **51**, 457—465).—It has already been shown that acenaphthylene yields decacyclene when heated at 280—290° (A., 1914, i, 826). In the hope of obtaining larger quantities of the latter hydrocarbon, other condensations in this field have been investigated, and it is now shown that both compounds can be prepared most conveniently by heating acenaphthene with lead oxide in a sealed tube. A third hydrocarbon is also formed in small quantities by this method. Being deep green in colour, it is designated chlorene .

For the preparation of decacyclene, $C_{36}H_{18}$, acenaphthene (10 grams) is heated with lead oxide (3·5) for three to four hours at 370—380° in a Carius tube. Unchanged acenaphthene is removed by boiling the product with alcohol, greenish-brown impurities by means of cold benzene, most of the fluorocyclene by boiling benzene, and most of the decacyclene by boiling cumene. The yield of the latter is 30—35%. For the preparation of fluorocyclene in a yield of as much as 25%, acenaphthene is heated with three times its weight of lead oxide for twenty hours at 330—340°, the tube being cooled to 110° every few hours and opened to let the steam escape. Fluorocyclene, $C_{48}H_{28}$, crystallises in small, orange-yellow rhombohedra belonging to the triclinic system, m. p. 396—397°.

The third hydrocarbon is found among the greenish-brown "impurities" and is formed in largest amount by heating acenaphthene with three times its weight of lead oxide for five to eight hours at 350°. It is isolated by protracted treatment with benzene and light petroleum in the cold, being more soluble in the mixture than certain yellow by-products. *Chlorene*, $C_{48}H_{26}$, crystallises in small, dark green scales, which shrink at about 265°, but are not molten at 300°. Dilute solutions are pure deep green in colour, but become brownish-red on exposure to sunlight. Concentrated solutions appear purple-red by a bright transmitted light. The spectrum shows the following absorption bands: $\lambda = 648—600\ \mu\mu$, very dark

and well defined; 550—546, much paler; 490 to the end of the visible violet, a faint band. J. C. W.

The Replacement in Amides of an Alkylanilino-group by an Aniline group by Heating with Aniline Hydrochloride. G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 983—985).—When 2 molecules of aniline are heated at 190° with 1 molecule of phenylmethylcarbamyl chloride, *s*-diphenylcarbamide is obtained. This substance is also formed when methyl carbanilide is heated with aniline hydrochloride. Replacement of the alkylaniline group is also found to occur when dimethyl- and diethyl-carbanilides are heated with aniline hydrochloride, and in similar circumstances, dimethyloxanilide gives oxanilide.

The replacement does not take place at lower temperatures, for when an ethereal solution of 1 molecule of phenylmethylcarbamyl chloride is heated with 2 molecules of aniline, the product obtained is methylcarbanilide. H. M. D.

Production of Aryl Sulphites. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 303033, 1916; from *Chem. Zentr.*, 1918, i, 499). —Aromatic sulphites are obtainable by treating aromatic hydroxyl compounds with thionyl chloride in the presence of pyridine or other suitable organic bases; the hydroxy-acids do not show this behaviour. Phenyl sulphite, b. p. 185°/15 mm. (in hydrogen); o-*tolyl sulphite*, $SO(O{\cdot}C_6H_4Me)_2$, b. p. 192° (corr.)/13 mm.; m-*tolyl sulphite*, b. p. 195—196° (corr.)/12 mm.; and p-*tolyl sulphite*, b. p. 199° (corr.)/12 mm., were obtained by the interaction of phenol or the cresol with thionyl chloride in the presence of pyridine and carbon disulphide; they are very stable towards water and aqueous alkalis, whereas some of their homologues, especially such as contain negative groups, readily undergo decomposition. The following compounds of this type were also prepared: *thymyl sulphite*, $SO(O{\cdot}C_6H_3Pr^{\beta}Me)_2$; *α-naphthyl sulphite*, $SO(O{\cdot}C_{10}H_7)_2$, indistinct crystals, m. p. 92—93°; *β-naphthyl sulphite*, nacreous powder, sensitive to water; p-*chlorophenyl sulphite*, $SO(O{\cdot}C_6H_4Cl)_2$, b. p. 213—214°/12 mm., solidifiable to a crystalline solid. D. F. T.

[**p-Acetylaminophenyl Allyl Ether.**] SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1263238).—p-*Acetylaminophenyl allyl ether*, leaflets, m. p. 94°, readily soluble in alcohol, ether, or acetone, but less readily so in hot water, acts as a narcotic, having also sedative and antineuralgic properties. T. F. B.

[**Preparation of Bromodiethylacetylurethanes of N-Acylated p-Aminophenols.**] FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Brit. Pat. 114680; U.S. Pat. 1256293 [SYNTHETIC PATENTS Co.]).—Compounds of the general formula

$$CEt_2Br{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}O{\cdot}Aryl{\cdot}NH{\cdot}Acyl,$$

are obtained by the interaction of *N*-acyl derivatives of *p*-aminophenols and bromodiethylacetylcarbimide, or of *p*-acylaminophenol-

urethanes and bromodiethylacetyl haloids. The *bromodiethylacetyl-urethane* of *p*-acetylaminophenol, white leaflets, m. p. 144°, is almost tasteless, and is readily soluble in alcohol or acetone, sparingly so in benzene, ether, or water. The bromodiethylacetyl-urethane of *p*-hydroxyphenylcarbamide melts at 187°. The compounds are of value as nervines and sedatives. A. S.

Compounds of Bivalent Cobalt with Catechol. R. F. WEINLAND and ANNA DÖTTINGER (*Zeitsch. anorg. Chem.*, 1918, **102**, 223—240).—Compounds have already been described in which the catechol residue ($C_6H_4O_2$) is combined with ferric iron (A., 1912, i, 184, 445) or aluminium (A., 1914, i, 525) to form a complex anion. A series of similar catechol derivatives containing cobalt is now described, a number of ammonium, pyridine, and potassium salts of the complex acid having been prepared. The salts are obtained, in general, by addition of alkali or base to an aqueous *solution containing catechol and a suitable cobalt salt, for example,* sulphate or acetate, in the requisite proportions. The composition of the precipitated salt depends principally on the quantity of base or alkali added; one or two molecular proportions of alkali throw down the complex cobalto-acid, whilst increasing quantities transform this into a complex salt.

The following five compounds were obtained when ammonia was used as a precipitant. In the formulæ, R stands for the catechol residue ($C_6H_4O_2$):

I. $[CoR_2]H_2,5\frac{1}{2}H_2O$, bright red, four- or six-sided prisms, sparingly soluble in water. It is produced by the further action of ammonia on V.

II. $[CoR_2](NH_4)_2$, red, slender, rectangular prisms, very sparingly soluble in water. It is formed by the action of excess of ammonia on V.

III. $3[CoR_2]H\cdot NH_4+[CoR_2](NH_4)_2,H_2O$, bright red crystal aggregates, sparingly soluble in water. The salt is stable in contact with its mother liquor, but quickly decomposes after separation therefrom.

IV. $[CoR_3](NH_4)_4,C_6H_4(OH)_2$, pale red, thin tablets, easily soluble in water. The isolation of this and the previous compound requires special precautions, for which the original must be consulted.

V. $Co_3R_2(OH)_2,6H_2O$, a pale red, sparingly soluble powder, always precipitated first when ammonia is added to a solution containing catechol and a cobalt salt.

Only a single compound was obtained when pyridine was substituted for ammonia.

VI. $4[CoR_2]H_2,(C_5H_5N)_2,C_6H_4(OH)_2$, a sparingly soluble, flesh-coloured, minutely crystalline precipitate.

Compounds I. and V. can both be obtained by addition of potassium hydroxide solution in limited quantity to a catechol-cobalt solution. Using increased quantities of the hydroxide, two potassium salts were obtained.

VII. $[CoR_2]KH,2H_2O$, red to bluish-violet, thin oblong tablets, easily soluble in water to a dirty green solution.

VIII. $[CoR_3]K_4,4H_2O$, red, slender, four-sided, rectangular prisms, very soluble in water. The salt is formed only in very strongly alkaline solutions ($1Co:3C_6H_4(OH)_2:40KOH$).

By merely warming a solution of cobalt acetate with catechol, a red, crystalline precipitate is formed, but this has not been investigated.

All the above compounds darken quickly on exposure to air, except the pyridine salt. They are stable to alkalis, in which they dissolve with a reddish-violet colour. Ammonium sulphide decomposes them with precipitation of cobalt sulphide, and they are also decomposed on boiling with potassium cyanide, potassium cobalticyanide being formed. The complex cobalt-catechol anion is, therefore, less stable than the ferri-catechol anion, which is not decomposed by these reagents. The cobalto-salts do not show the intense colour characteristic of the ferric salts.

The constitution of the salts is discussed and co-ordination formulæ are suggested. E. H. R.

Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. II. RALPH C. HUSTON and THEODORE E. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1918, **40**, 785—793. Compare A., *1917*, i, 19).—When aluminium chloride is added to a mixture of phenylmethylcarbinol and benzene at such a rate that the temperature is maintained at 25—35°, the reagents being in molecular proportions, *as*-diphenylethane is obtained in approximately 20% yield, together with ethylbenzene, diphenylmethane, and anthracene, these by-products being formed by the further action of aluminium chloride. By keeping the temperature below 10° and using only a semi-molecular proportion of aluminium chloride and a five-fold molecular proportion of benzene, the yield of diphenylethane is raised to 65%.

Phenylethylcarbinol, benzene, and *aluminium chloride in molecular* proportions at 35—40° yield 23—25% of *αα*-diphenylpropane, together with propylbenzene, diphenylmethane, and anthracene; by modifying the conditions, as in the preceding case, the yield of diphenylpropane can be raised to 40% of the theoretical.

Benzhydrol reacts with benzene (5 *mols.*) and *aluminium* chloride (1 mol.) at 35—40°, giving a yield of 40% of triphenylmethane, accompanied by diphenylmethane; with the reaction effected below 10°, the yield of triphenylmethane is 65—70%.

D. F. T.

Preparation of a Derivative of Hexamethylenetetramine. LEO EGGER (D.R.-P., 303450, 1915; from *Chem. Zentr.*, 1918, i, 499).—Hexamethylenetetramine *o*-acetoxybenzoate,

$$OAc\cdot C_6H_4\cdot CO_2\cdot C_6H_{12}N_4,$$

m. p. 118—119°, is prepared by the gradual addition of hexamethylenetetramine (1 mol.) to a solution of *o*-acetoxybenzoic acid (1 mol.) in a restricted volume of ether. D. F. T.

Preparation of Tropic Acid. CHEMISCHE WERKE GRENZACH (D.R.-P., 302737, 1917; from *Chem. Zentr.*, 1918, i, 396).—Ethyl hydroxymethylenephenylacetate is reduced to ethyl tropate and hydrolysed, the resulting tropic acid being identical with the product obtained from atropine. D. F. T.

A New Method for the Preparation of Aldehydes. I. KARL W. ROSENMUND (*Ber.*, 1918, **51**, 585—594).—The author has discovered the conditions whereby acyl chlorides can be converted into the corresponding aldehydes by means of hydrogen in the presence of a catalyst. The method gives excellent results and promises to be the best yet devised for the preparation of aldehydes.

The best conditions are far from what might have been predicted. The most suitable catalysts are palladinised barium sulphate containing about 5% of metal, and Kelber's nickel catalyst (A., 1917, ii, 215). The chloride is dissolved in three to five times its volume of dry xylene or cumene, which are usually regarded as "poisonous" to catalysts, and the solution is actually boiled in a reflux apparatus, hydrogen being bubbled through the while and the hydrogen chloride escaping. Even if the chloride contains traces of phosphoryl chloride, the reduction proceeds smoothly. The aldehyde is subsequently removed by means of sodium hydrogen sulphite or distillation, and the yields are often very high.

As examples, the following preparations are described; benzaldehyde from benzoyl chloride, yield 97%; butyraldehyde from butyryl chloride, yield 50%; stearaldehyde from stearyl chloride; p-*methylcarbonatobenzaldehyde*, $CO_2Me{\cdot}O{\cdot}C_6H_4{\cdot}CHO$, radial aggregates of needles, m. p. 18·5° (*phenylhydrazone*, m. p. 157—158°), from *p*-methylcarbonatobenzoyl chloride, yield 95%. J. C. W.

A New Method for the Preparation of Aldehydes. II. Synthesis of Gallaldehyde. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1918, **51**, 594—602).—The carbomethoxy- and acetyl derivatives of gallic acid are converted into the chlorides, these reduced to the aldehydes by the new method (preceding abstract), and then hydrolysed to gallaldehyde.

3:4:5-*Trimethylcarbonatobenzaldehyde*, $CHO{\cdot}C_6H_2(O{\cdot}CO_2Me)_3$, is a resinous mass, and its p-*nitrophenylhydrazone* is also viscous. 3:4:5-*Triacetoxybenzaldehyde*, from triacetylgalloyl chloride (this vol., i, 173), is also resinous, but its p-*nitrophenylhydrazone* separates in lemon-yellow, cruciform groups of fan-like crystals, m. p. 186—187° (decomp.). These aldehydes are hydrolysed in an atmosphere of hydrogen, the former by means of 2*N*-sulphuric acid at 0°, the latter by boiling with alcoholic potassium acetate. *Gallaldehyde* (3:4:5-*trihydroxybenzaldehyde*) crystallises from water with $1H_2O$, which it slowly loses in a desiccator, becoming yellow. It has m. p. 212° (decomp.), does not precipitate gelatin, reduces ammoniacal silver and Fehling's solutions immediately, develops a golden-yellow colour when shaken with calcium cyanide solution, and an inky-blue with ferric chloride. The p-*nitro-*

phenylhydrazone forms golden-yellow, feathery needles, m. p. 234—236° (decomp.), but the aldehyde is so strongly acidic that it also yields a p-*nitrophenylhydrazine* salt of its p-*nitrophenylhydrazone*, in bundles of stout, yellowish-red needles, m. p. 202—204° (decomp.). On methylation with methyl sulphate, the aldehyde yields the known 3 : 4 : 5-trimethoxybenzaldehyde (Mauthner, A., 1908, i, 348).

Nierenstein (A., 1909, i, 402) believed he had isolated gallaldehyde by the hydrolysis of acetylleucotannin, but according to his account it separated spontaneously from a solution containing not more than 1% of the aldehyde in alkali carbonate. As the aldehyde is more acidic than acetic acid, and freely soluble in water and alkali carbonates, it is improbable that Nierenstein encountered the compound. J. C. W.

Preparation of Salts of Anthraquinonesulphonic Acids. THE BARRETT Co. (U.S. Pat. 1260535).—Anthraquinonemonosulphonic acid may be separated from the disulphonic acids by treating a solution of the acids with sodium sulphate, whereon the monosulphonic acid is precipitated as its sparingly soluble sodium salt. A. S.

Constituents of Essential Oils. Betulol. F. W. SEMMLER, K. G. JONAS, and W. RICHTER (*Ber.*, 1918, **51**, 417—424).—From an examination of betulol, an ingredient of birch bud oil (compare von Soden and Elze, A., 1905, i, 451), the conclusion is drawn that the compound is a bicyclic sesquiterpene alcohol of the terpene type.

Betulol, $C_{15}H_{24}O$, has b. p. 157—158°/13 mm., D^{16} 0·9777, n_D^{16} 1·5150, a_D^{16} −26·5°, and betulyl acetate (*ibid.*) has b. p. 158—165°/10 mm., D^{20} 0·9854, n_D^{20} 1·4962, $[a]_D^{20}$ −12°. Betulol slowly absorbs hydrogen in the presence of platinum, yielding *tetrahydrobetulol*, b. p. 153—158°/14 mm., D^{18} 0·9415, n_D^{18} 1·4908, a_D^{18} −6·8°, and a small quantity of bicyclic *tetrahydrobetulene*, $C_{15}H_{28}$, b. p. 118—120°/11 mm., D^{18} 0·8737, n_D^{18} 1·4744, a_D^{18} −3°, this being derived from the product of the elimination of water from betulol. *Betulyl chloride*, obtained by means of phosphorus pentachloride, has b. p. 160—170°/11 mm., D^{21} 1·0145, n_D^{21} 1·5208, a_D^{21} +9·4°, but this is obviously a mixture, for it yields an inseparable mixture of bi- and tri-cyclic *betulenes*, $C_{15}H_{24}$, on pouring its alcoholic solution on hot sodium. The molecular refraction of the latter mixture affords the clue to this, and it is explained by the fact that hydrogen chloride, generated during the action of the phosphorus pentachloride, effects ring closure to a certain extent. Treatment of the chloride with calcium oxide at 95° also indicates the presence of a mixture, for the products are bicyclic *dehydrobetulene*, $C_{15}H_{22}$, b. p. 112—114°/9 mm., D^{23} 0·9186, n_D^{23} 1·5052, a_D^{23} −68°, and tricyclic *betulol*, $C_{15}H_{24}O$, which crystallises in silky needles, m. p. 147—148°, b. p. 160—166°/13 mm., and forms an *acetate*, b. p. 170—176°/13 mm., D^{22} 1·0290, n_D^{22} 1·5046, a_D^{22} +10°. J. C. W.

Japanese Oil of Peppermint. HEINRICH WALBAUM (*J. pr. Chem.*, 1917, [ii], **96**, 245—250).—By the hydrolysis of the fraction of Japanese peppermint oil, b. p. 250—310°, D^{15} 0·9490, there is obtainable *Δγ-hexen-α-ol*, CHEt:CH·CH_2·CH_2·OH, b. p. 55—56°/9 mm., 156—157°/atmos. press., D^{15} 0·8508, n_D^{20} 1·48030, the constitution of which is proved by its oxidation with potassium permanganate to propionic acid; *Δβ-hexenaldehyde*, b. p. 140—155° (*semicarbazone*, m. p. 163°), and the oily Δβ-hexenoic acid, b. p. 215—218° (Fittig and Baker, A., 1895, i, 206, give b. p. 216—217°), are also obtained, together with the hexenyl hexenoate, on oxidation of the alcohol with chromic acid. The hexenyl alcohol is present in the peppermint oil in the form of *Δβ-hexenyl phenylacetate*, $C_{14}H_{18}O_2$; the pure, synthetically prepared ester is a liquid of clinging, onion-like odour, b. p. 135—136°/4 mm., 299°/760 mm., D^{15} 1·000, n_D^{20} 1·49810; the *benzoate*, b. p. 134—135°/6 mm., D^{15} 1·0083, n_D^{20} 1·50560, possesses a fainter odour than the phenylacetate; the *acetate*, b. p. 75—76°/23 mm., D^{15} 0·9077, n_D^{20} 1·42355, has a pleasant odour recalling radishes, whilst the *formate*, b. p. 66°/35 mm., D^{15} 0·9149, n_D^{20} 1·42685, has a similar but rather more pungent odour; the *hydrogen phthalate*, $C_{14}H_{16}O_4$, is an oil, the *silver* salt of which crystallises in prisms. With phenylcarbimide, the hexenyl alcohol yields no solid product, but when treated with naphthylcarbimide, a crystalline *naphthylurethane*, $C_{17}H_{19}O_2N$, m. p. 70—71°, is obtained. D. F. T.

Saponins. L. SPIEGEL and ARTHUR MEYER (*Ber. Deut. pharm. Ges.*, 1918, **28**, 100—126).—An examination of the saponin mowrin, obtainable from the seeds of *Bassia longifolia* (Mowrah seeds), the results of which diverge considerably from those of Moore, Sowton, Baker-Young, and Webster (A., 1910, ii, 228).

Crude mowrin consists mainly of a substance approximating to the composition $C_{42}H_{68}O_{25}$, easily soluble in alcohol, together with a sparingly soluble substance approximating to $C_{42}H_{68}O_{27}$. On hydrolysis with aqueous mineral acid, the main constituent gives rise to lævulose, arabinose, and mowric acid, the latter comprising a crystalline *mowragenic acid*, $C_{19}H_{28}O_5$ (*sodium* salt sparingly soluble), and an amorphous, *mowrageninic acid*, $C_{19}H_{30}O_6$. By effecting the hydrolysis of mowrin with dilute acetic acid, it is possible to detect an intermediate product, namely, a pentoside, probably of the composition $C_{29}H_{50}O_{16}$. The ease with which mowrin undergoes hydrolysis is shown by the fact that on benzoylation it and mowric acid yield the same benzoyl derivative, whilst the product obtained on acetylating mowrin with sodium acetate and acetic acid appears to be derived from the above intermediate pentoside compound.

On treatment with manganese dioxide and sulphuric acid, mowric acid undergoes oxidation and polymerisation with formation of *didehydromowric acid*, $C_{38}H_{48}O_9$, m. p. 163°, whereas hot 35% nitric acid produces *nitrodehydromowric acid*, $C_{19}H_{23}O_5$·NO_2, m. p. 207°, the reduction of which with stannous chloride gives a *hydroxydehydromowric acid*, $C_{19}H_{23}O_5$·OH, m. p. 200° (*trimethyl* deriv-

ative, m. p. 183°; *diethyl* derivative, m. p. 136°). More energetic nitration of mowric acid gives rise to a nitro-compound, $C_{17}H_{21}O_5{\cdot}NO_2$ or $C_{17}H_{19}O_5{\cdot}NO_2$, m. p. 210°, which is reducible to a hydroxy-*compound*, $C_{17}H_{19}O_5{\cdot}OH$, m. p. 170° (*trimethyl* derivative, m. p. 142°; *diethyl* derivative, m. p. 150°). This nitro-compound is oxidisable by hydrogen peroxide and by potassium permanganate with sulphuric acid, giving substances $C_{17}H_{18}O_5(OH)_2$, m. p. 125°, and $(C_{17}H_{19}O_6)_2O$, m. p. 164°, respectively, whilst hydriodic acid converts its reduction product into a substance $C_{17}H_{21}O_5I$ or $C_{17}H_{23}O_5I$, m. p. 174°. Fusion with potassium hydroxide converts mowric acid into a *substance* $C_{14}H_{18}O_3$, m. p. 181° (*methyl* deriv-ative, m. p. 160—175°). D. F. T.

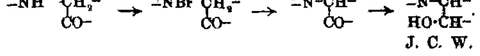
The Action of Sunlight on Coumarin. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 875—876. Compare Ciamician and Silber, A., 1914, ii, 234).—A preliminary account of experiments which indicates that the product of sun-light on coumarin is not the hydrodicoumarin which was obtained synthetically by Fittig and Dyson in 1889 (compare Dyson, T., 1887, **51**, 66). S. B. S.

Synthesis of Pyranol Derivatives. SARAT CHANDRA CHATTERJI and BROJENDRA NATH GHOSH (T., 1918, **113**, 444—449). —Diketohydrindene condenses with *o*-hydroxyaldehydes, giving ketoindopyranol derivatives (compare T., 1915, **107**, 1442), this reaction being due, apparently, to the presence of the group $\cdot CO\cdot CH_2\cdot CO\cdot$ in the diketohydrindene. In order to show that the reaction is a general one, two other ketones, benzoylacetone and acetylacetone, containing this group have been condensed with salicylaldehyde.

Benzoylacetone, when condensed with salicylaldehyde in methyl alcohol solution in the presence of hydrogen chloride, gave 3-*acetyl-2-phenyl*-1:4-*benzopyranol anhydrohydrochloride* and 3-*benzoyl-2-methyl*-1:4-*benzopyranol anhydrohydrochloride*, together with a third *compound*, $C_{27}H_{20}O_3,\frac{1}{2}H_2O$, m. p. 120°.

With acetylacetone, salicylaldehyde gave a *compound*, $C_{17}H_{18}O_3$, violet prisms soluble in acetic acid, giving a *hydrochloride*, a *phenylhydrazone*, m. p. above 300°, and an insoluble *compound*, $C_{24}H_{22}O_6$. [For experimental details, see the original.] W. G.

The Cinchona Alkaloids. XIX. Partial Synthesis of Quinine. PAUL RABE and KARL KINDLER (*Ber.*, 1918, **51**, 466—467. Compare A., 1911, i, 742).—Quinicine (quinotoxine) reacts with sodium hypobromite to form N-*bromoquinicine*, m. p. 123°. This is converted into quininone by treatment with alkali hydroxide, and the ketone is reduced to quinine by means of aluminium powder and sodium ethoxide solution. Considering only the groups affected, the synthesis is represented thus:



J. C. W.

α-Hydroxycinchonine. E. Léger (*Compt. rend.*, 1918, **166**, 903—906).—As a result of a study of the behaviour of α-hydroxycinchonine (compare Jungfleisch and Léger, A., 1888, 380, 508; 1889, 906), the author considers that the hydroxyl group is in the side chain, the double linking in the vinyl group being satisfied during the process of hydration. α-Hydroxycinchonine thus has the constitution CH_3·CH(OH)·[$C_{16}H_{17}$(CH·OH)N_2]. The grouping CH_3·CH(OH)· is preferred to CH_2(OH)·CH_2·, since the compound yields (1) iodoform by the action of sodium hydroxide and iodine, and (2) carbon tetrabromide by the action of hypobromous acid.

W. G.

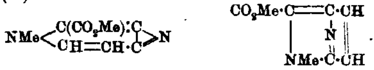
Cevadine [Veratrine]. III. Martin Freund and Adolf Schwarz (*J. pr. Chem.*, 1917, [ii], **96**, 236—244. Compare A., 1904, i, 613).—As the author has been unable to confirm the results described earlier (*Zeitsch. Ver. deutsch. Chem.*, 1909, **22**, 2472) on the degradation of cevine, these are withdrawn. When cevine methiodide, $C_{27}H_{43}O_8N$,MeI,$2H_2O$, decomp. 257° (Freund and Schwarz, A., 1899, i, 465), is treated with silver oxide and water, it undergoes conversion into des-N-*methylcevine*, $C_{28}H_{45}O_8N$,H_2O, crystalline scales, decomp. at 277° (accompanied by an uncrystallisable yellow oil), which absorbs atmospheric carbon dioxide, with formation of a hydrogen carbonate, and yields crystalline salts resistant to aqueous ammonia or sodium carbonate; the *hydriodide* ($1H_2O$), decomp. at 256°, *hydrobromide*, with $1H_2O$, decomp. at 271—273°, *hydrochloride*, decomp. at 258—261°, and *picrate*, with $3H_2O$, were prepared. Methyl iodide at 60—70°, cyanogen bromide, phenylhydrazine, hydroxylamine, semicarbazide, thiosemicarbazide, and aqueous hydrogen peroxide left the cevine molecule intact. Treatment of a methyl-alcoholic solution of de-*N*-methylcevine hydrochloride with silver oxide yields an alkaline solution, which, on evaporation, leaves an oily residue; this, on the addition of alkali and warming, changes into the crystalline solid base, the behaviour being suggestive of a tautomeric change from a true ammonium base to a pseudo-base.

Examination of cevadine, cevine, and dibenzoylcevine by Zerewitinoff's method with a solution of methyl magnesium iodide in *iso*amyl ether indicates the presence of four, six, and six hydroxyl groups respectively, the unexpected value for the last figure being at present without explanation.

D. F. T.

Ricinine. Bruno Böttcher (*Ber.*, 1918, **51**, 673—687).—The most important study of ricinine, the alkaloid of castor-oil seeds, which has appeared so far is that by Maquenne and Philippe, who went so far as to assign the formula (I) to the compound (A., 1905, i, 80). In view of the very unusual three-membered nitrogen-carbon ring in this formula, the author has

made a fuller examination of ricinine, and proposes the formula (II):



(I.) (II.)

This accords with the behaviour of ricinine at one and the same time as the ester of a pyridinecarboxylic acid and as a glyoxaline.

The alkaloid is obtained by extracting the residue of the seeds with boiling water, after removing the oil, evaporating the extract to dryness under reduced pressure, and exhausting the powder with alcohol. From 300 kilos. of seed, about 450 grams of crude alkaloid may be obtained. The pure compound has m. p. 200—201°, reduces permanganate at once, is not affected by nitric acid, and, like histidine, gives Weidel's reaction. On hydrolysis with dilute potassium carbonate, it yields ricininic acid, m. p. 296—298° (decomp.), which forms a *silver* salt, from which ricinine may be recovered by means of methyl iodide. The acid may be reduced by means of 5% sodium amalgam to *dihydroricininic acid*, which crystallises from water in white needles, m. p. 245° (if quickly heated), 255° (if slowly heated), which give an intense violet coloration with ferric chloride, characteristic of glyoxaline-carboxylic acids. The *methyl* ester (*dihydroricinine*), prepared from the *silver* salt, but not by reducing ricinine itself, crystallises in glistening needles or plates, m. p. 160°, and is much more easily hydrolysed than ricinine. The failure to obtain a tetrahydro-derivative is an argument in favour of formula (II) as against (I); the ethylene linking in the glyoxaline ring is, as usual, unaffected by sodium amalgam.

Ricininic acid is oxidised by chromic acid and dilute sulphuric acid to methylamine, oxalic acid, and hydrogen cyanide, the evolution of this being quantitative, one molecule per molecule of acid, and characteristic also of histidine. Hypobromite *solutions apparently cause saturation of the ethylene linking, a compound*, m. p. 256—257° (decomp.), represented by the formula $HBrO,C_7H_6O_2N_2$ (ricininic acid), crystallising on acidifying. Distillation with zinc dust furnishes a dipyridyl (*aurichloride*, $C_{10}H_8N_2,HAuCl_4$, decomp. 250°) and a pyrrole derivative. Distillation with lime also gives a pyrrole compound, which is another established reaction of histidine.

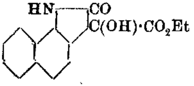
Ricininic acid is degraded to 3-hydroxy-1-methyl-1:4-dihydropyrid-4-one, $NMe<\begin{matrix}CH{=}CH\\CH{:}C(OH)\end{matrix}>CO$, by means of fuming hydrochloric acid at 150° (the best method; see Maquenne and Philippe, A., 1904, i, 339), or by hydrolysis with alkali hydroxides. If heated with 50% sulphuric acid, an *acid* is produced, m. p. 216° (decomp.), which contains one NMe group, gives the reddish-brown colour with ferric chloride characteristic of pyridine-carboxylic

acids, yields a pyrrole on distillation with lime, and forms the above pyridone on heating with hydrochloric acid at 150°. The pyridone does not give the pyrrole reaction on distillation with lime. J. C. W.

Synthesis of α-Piperidylethylalkine (2-α-Hydroxypropylpiperidine). LUDWIG LAUTENSCHLÄGER and ARVID G. T. ONSAGER (*Ber.*, 1918, **51**, 602—605).—Pyridine-2-aldehyde (Harries and Lénárt, A., 1915, i, 970) is converted into 2-α-hydroxypropylpyridine, b. p. 214—216° (Engler and Bauer, A., 1891, 1505) by means of magnesium ethyl bromide, and this is reduced by sodium and alcohol to 2-α-hydroxypropylpiperidine, which crystallises from light petroleum in leaflets, m. p. 99—100°, and needles, m. p. 69—70° (*ibid.*, 1894, i, 471). A small quantity of *r*-coniine is formed as well. J. C. W.

Transformation of Unimolecular *N*-Alkyldihydroquinaldine Picrates. GUSTAV HELLER (*Ber.*, 1918, **51**, 437—439).—The picrates of 1 : 2-dimethyl- and 2-methyl-1-ethyl-1 : 2-dihydroquinoline (A., 1915, i, 300; and Freund, A., 1905, i, 151; 1909, i, 417) suffer rearrangement on crystallisation from acetone and light petroleum into bright red *isomerides* (1-methyl-, m. p. 148°; 1-ethyl-, m. p. 128°). These do not yield the parent bases on treatment with sodium hydroxide, but change into the *sodium* salts of third, acidic *isomerides* (1-methyl-, m. p. 129—131°; 1-ethyl-, m. p. 136°; both pale brown granules). J. C. W.

Synthesis in the α-Naphthindole Series. J. MARTINET (*Compt. rend.*, 1918, **166**, 851—853. Compare A., 1913, i, 756).—α-Naphthylamine condenses with ethyl mesoxalate in boiling acetic acid solution to give *ethyl 3-hydroxy-2-oxynaphthindole-3-carboxylate* (annexed formula), m. p. 201°. The corresponding *methyl* ester has m. p. 268°. Either of these esters, when heated in a water-bath with aqueous potassium hydroxide in a current of hydrogen, and the liquid then acidified, yields *α-naphthoxindole*, m. p. 247°. These esters, when treated with aqueous potassium hydroxide in contact with air, yield potassium α-naphthisatate, from which, when the solution is acidified, α-naphthisatic acid is precipitated, which is rapidly converted into α-naphthisatin, red needles, m. p. 225° (compare Hinsberg, A., 1888, 373). Contrary to the statement of Hinsberg (*loc. cit.*), this isatin gives the indophenine reaction, and its phenylhydrazone has m. p. 286°, and not 270°, as stated (*loc. cit.*).

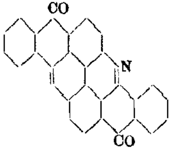


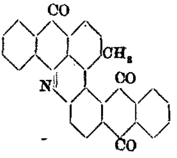
W. G.

Preparation of Mercury Compounds of the Acridine Series. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1259517).—The mercury compounds obtained by treating acridine dyes, alkylated at the acridine nitrogen atom, with a soluble mercury salt in the presence of a solvent, are yellowish-brown powders,

giving yellowish-green solutions in water, yellowish-green fluorescence in dilute solution in alcohol, ethyl acetate, glacial acetic acid, and acetone, and an intense green fluorescence in concentrated sulphuric acid. Even in very dilute solutions they check the growth of bacteria. The mercury compound of the product obtained by heating 3:6-diamino-2:7-dimethylacridine with methyl chloride under pressure, is specially claimed. A. S.

Pyranthridone. ROLAND SCHOLL and OTTO DISCHENDORFER (*Ber.*, 1918, **51**, 441—452).—Pyranthridone (annexed formula) may be regarded as a compound intermediate between pyranthrone, $C_{30}H_{14}O_2$, and flav-*anthrene*, $C_{28}H_{12}O_2N_2$. Its *synthesis* is now described. 1-Chloro-2-aminoanthraquinone (A., 1913, i, 1070) is boiled with benzaldehyde, the water produced being allowed to escape, when *1-chloro-2-benzylideneaminoanthraquinone* is formed, in pale yellow leaflets, m. p. 184°. This is boiled with 1-chloro-2-methylanthraquinone in naphthalene solution, with a little copper powder, when a mixture of dianthraquinonyls is obtained, consisting of condensation products of each of the reacting compounds separately and the desired unsymmetrical 2-benzylideneamino-2′-methyl-1:1′-dianthraquinonyl. After removing the solvent naphthalene by steam, the residue is dissolved in concentrated sulphuric acid, whereby the 2:2′-dimethyl-1:1′-dianthraquinonyl is unchanged, but the benzylidene residues from the other products are eliminated as benzaldehyde. The 2:2′-diamino-1:1′-dianthraquinonyl so formed immediately condenses to flavanthrene and the 2-amino-2′-methyl-1:1′-dianthraquinonyl to *3:4-phthalyl-8:9-o-benzoylene-5-methylphenanthridine* (annexed formula). The latter is moderately soluble in hot nitrobenzene, whereas flavanthrene is almost insoluble, and the other products are freely soluble. It crystallises in golden, rhombic leaflets, which do not melt below 450°. Reduction with hyposulphite at 30—40° gives a red vat, from which a *di-p-bromobenzoyl* derivative,





$C_{29}H_{15}ON(O\cdot CO\cdot C_6H_4Br)_2$,

small, yellow needles, m. p. 318°, may be prepared, whilst reduction with strongly alkaline solutions of hyposulphite at higher temperatures yields a blue vat, from which a *di-p-bromobenzoyl-*derivative, $C_{29}H_{17}ON(O\cdot CO\cdot C_6H_4Br)_2$, m. p. 210°, may be obtained.

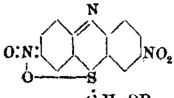
The phenanthridine derivative may be condensed to *pyranthridone* by heating alone at 360—380°, or with sulphuric acid at 160—170°, or with alcoholic potassium hydroxide. The dye crystallises from quinoline in brownish-yellow needles, which sublime on heating, but are not molten at 500°. It yields a violet-blue

vat, from which cotton is dyed orange-red after hanging in the air. A *di*-p-*bromobenzoyl* derivative, felted, orange-yellow needles, decomp. 350°, may also be obtained from the tetrahydro-compound in the vat. When heated with hydriodic acid and phosphorus, pyranthridone yields *dihydropyranthridine*, $C_{29}H_{19}N$, in pale yellow, rhombic leaflets, m. p. 302°, which is converted into the parent base, *pyranthridine*, $C_{29}H_{17}N$, reddish-brown leaflets, m. p. 370°, by passing its vapour over red-hot copper. J. C. W.

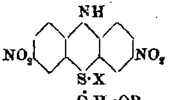
Synthesis of Flavanthrene. R. Scholl and O. Dischendorfer (*Ber.*, 1918, **51**, 452—453).—The immediate precursor of flavanthrene in the various syntheses which have been achieved is 2:2′-*diamino*-1:1′-*dianthraquinonyl*, but this has not hitherto been isolated. It may be prepared by boiling 1-chloro-2-benzylideneaminoanthraquinone with copper powder and naphthalene (compare preceding abstract), extracting the 2:2′-dibenzylideneamino-1:1′-dianthraquinonyl so formed with cold alcohol, and leaving the solution for some time, when the benzylidene residues are spontaneously eliminated and the desired compound crystallises. It forms microscopic, red needles, and changes into flavanthrene at 250°. J. C. W.

The Properties of the Sulphonium Compounds obtained by S. Smiles by the Condensation of Dinitrophenthiazinesulphoxide with Aromatic Amines, Phenols, and Phenol-ethers. F. Kehrmann, S. Lievermann, and P. Frumkine (*Ber.*, 1918, **51**, 474—480).—A revision and criticism of the work of Smiles and Hilditch (T., 1908, **93**, 145). It appears that the products obtained by these workers were abnormally coloured by impurities, although their constitution was rightly interpreted.

It is essential to use pure 3:9-dinitrophenthiazinesulphoxide, prepared as in A., 1913, i, 1231, for the condensations, and the reaction with anisole or phenetole is best brought about by shaking a mixture of the compounds with concentrated sulphuric and acetic acids (1:1). The phenazothionium salts so produced are converted into the free bases by precipitation with ammonia. 3:9-*Dinitro*-1-*anisylphenthiazine*, m. p. 248°, forms carmine-red flocks, which change in contact with the mother liquor into a green, crystalline powder with metallic lustre, and the 1-*phenetyl* compound, m. p. 230°, crystallises in groups of fiery-red prisms or dark red granules with green lustre. The free bases resemble rosindone, and their solutions exhibit a brilliant orange-yellow fluorescence, whilst solutions of their salts are pale in colour and not fluorescent. The



(I.)



(II.)

free "bases" are therefore para-quinonoid, internal phenazothionium salts of nitronic acid (I), whilst the salts of mineral acids (II) contain nitro-groups as the sole chromophores.

The *chloride* of the anisyl derivative forms straw-yellow granules, the *platinichloride* is pale yellow, and the *dichromate* is egg-yellow.

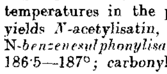
The anisyl compound has also been reduced by means of stannous chloride, the stannichloride so formed acetylated, and the new canary-yellow base, 3:9-*diacetylamino*-1-*anisylphenazothionium*, isolated as the *hydrogen carbonate*, which forms satiny scales, the *platinichloride* being very pale yellow. J. C. W.

Syntheses in the Isatin Series. "Definitive Enzymic Synthesis." GUSTAV HELLER (*Ber.*, 1918, **51**, 424—437).—*N*-Sodioisatin reacts readily with organic chlorides at moderate temperatures in the presence of benzene. Thus, acetyl chloride yields *N*-acetylisatin, m. p. 141°; benzenesulphonyl chloride gives N-*benzenesulphonylisatin*, in pale yellow, slanting prisms, m. p. 186·5—187°; carbonyl chloride forms *carbonyldi-isatin*,

$$\begin{matrix} C_6H_4— \\ CO·CO \end{matrix}>N·CO·N<\begin{matrix} —C_6H_4 \\ CO·CO \end{matrix},$$

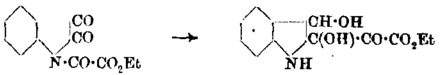
in long, yellow needles, m. p. 218° (decomp.); ethyl chloroformate yields *ethyl isatin*-1-*carboxylate*, in yellow prisms, m. p. 117°, which forms a *dioxime*, needles, m. p. 145°, and the corresponding *methyl* ester crystallises in golden-yellow leaflets, m. p. 170°.

The latter esters undergo a remarkable change when boiled with water, left with 50% sulphuric acid or concentrated hydrochloric acid, or treated with zinc dust and acetic acid. The product is an acid with four atoms of hydrogen more than the parent 1-carboxylic compound; it does not give the indophenine reaction, but it very readily yields isatinic acid when exposed in alkaline solutions to the air. Acetaldehyde is also produced if the ethyl ester is used, and formaldehyde from the methyl ester. The acid is therefore 2:3-*dihydroxy*-2:3-*dihydroindole*-2-*carboxylic acid* (annexed formula); it forms colourless crystals, m. p. 144°, and yields a *phenylhydrazide*, pale yellow, narrow prisms, m. p. 152° (decomp.), and a *lactone*, long, yellow needles, m. p. 108°. The corresponding esters, *ethyl*, m. p. 67°, and *methyl*, m. p. 85°, are produced when the original esters are boiled with the alcohols. Acetaldehyde and formaldehyde are also produced, but the origin of the four hydrogen atoms is obscure. As a rule, it is by no means easy to convert an indole derivative into a dihydroindole compound, but the above reaction indicates that when the carbalkyloxy-group is introduced into isatin, the subsequent fixation of as many as four atoms of hydrogen, and a thorough internal rearrangement in the molecule, become very easy. The change resembles the far-reaching effects so often produced by enzymes, and the fact that acids stimulate the change only strengthens the analogy.



The acid undergoes another remarkable change on oxidation with potassium dichromate and dilute sulphuric acid. The product is an acid which contains an extra methylene group and yields quinaldic acid on reduction with hydriodic acid and phosphorus. It is therefore 2:4-*dihydroxy*-1:2:3:4-*tetrahydroquinoline-2-carboxylic acid*, $C_6H_4<\begin{matrix}CH(OH)\cdot CH_2 \\ NH\text{———}C(OH)\cdot CO_2H\end{matrix}$; it forms long needles, m. p. 127°, yields a *methyl* ester, m. p. 62°, and gives a *hydroxydihydroquinoline-2-carboxylic acid*, m. p. 184°, on heating with acetic anhydride and sodium acetate. This obscure case of the extension of the ring from five members to six also recalls enzyme activities.

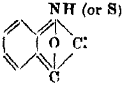
N-Sodioisatin also reacts with ethyl oxalyl chloride, forming N-*ethyloxalato-isatin* [*ethyl isatin*-1-*glyoxylate*] (A), in pale yellow needles, m. p. 180—182°, which changes into 2:3-*dihydroxy*-2-*ethyloxalatodihydroindole* [*ethyl* 2:3-*dihydroxy*-2:3-*dihydroindole*-2-*glyoxylate*] (B), m. p. 81°, when boiled with alcohol.



(A.) (B.)

J. C. W.

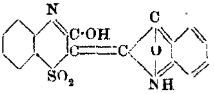
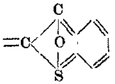
Dyes Derived from Sulphazone. A Contribution to Claasz's New Theory of the Indigo Chromophore. W. HERZOG (*Ber.*, 1918, **51**, 516—521).—Sulphazone, which does not form an oxime or hydrazone, thus agreeing with the suggestion that it should be regarded as 3-hydroxybenzsulphonazine (A., 1916, i, 424), has often been used as a component in azo-dyes (A., 1912, i, 390). It has also been converted into benzsulphonazoline by the action of ammonia under pressure (Claasz, A., 1916, i, 425), and this has been used to prepare dyes which closely resemble indigotin without containing the usually accepted indigo chromophore, –CO·C:C·CO–. The discovery of these dyes has led Claasz to suggest that the indigo chromophore is a quinonoid, inner-salt structure of the annexed type (A., 1916, i, 840).



It is now shown that sulphazone itself, because of its reactive methylene group, can also form vat-dyes of the indigoid type, the tinctorial properties of which can only be ascribed to the presence of the above chromophore.

Sulphazone condenses with *a*-isatinanilide in boiling acetic anhydride to form the *compound* (I). This separates in deep bluish-red crystals, which sublime at above 300°, and dissolve in concentrated sulphuric acid with violet colour and in fuming acid (20% SO_3) with carmine colour. It is decomposed by alkalis after a time, but a fresh, yellowish-green solution in sodium hydroxide yields a red and finally yellow hyposulphite vat. The affinity for fibres is very small, however, and the colour on

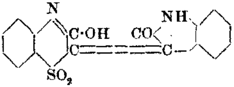
filter paper changes from strawberry-red to dark green, probably owing to the participation of the sulphonyl group in the reduction.

(I.) (II.)

The *compound* (II) is obtained by condensing sulphazone with thionaphthenequinone-anilide (A., 1908, i, 200). It forms yellowish-red needles which melt and sublime at above 300°, and although it is unstable towards alkali hydroxides, it is possible to prepare a yellow hyposulphite vat.

When sulphazone is condensed with β-isatinanilide (isatin-2-anil), a compound is produced which is related to the above dye (I) as indirubin is to indigotin. The lack of tinctorial properties is ascribed to the absence of the above chromophore. The *compound* (annexed formula) forms



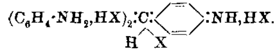
bluish-red crystals which decompose at about 300°, and dissolve in *sulphuric acid with yellowish- to reddish-brown colour.* J. C. W.

Hydantoin Derivatives. Clarence J. West (*J. Biol. Chem.*, 1918, **34**, 187—194).—The following hydantoin derivatives have been prepared by the method described by Dakin (A., 1910, i, 590). In view of Dakin's theory regarding the structure of allantoin (T., 1915, **107**, 434), it was thought that the active *dl*-hydantoins might be found to differ in physical properties from the inactivated forms. Such differences have not been observed. d-*a-Phenylcarbamidopropionic acid*, $C_{10}H_{12}O_3N_2$, crystallises in needles, m. p. 175° (decomp.), $[\alpha]_D^{20}$ +7·78° in acetone; d-*a-phenylmethylhydantoin*, $C_{10}H_{10}O_2N_2$, m. p. 178°, $[\alpha]_D^{20}$ +2·24° in *N*/2-sodium hydroxide and −10·04° in acetone; dl-*a-naphthylmethylhydantoin*, $C_{14}H_{12}O_2N_2$, m. p. 179—180°; d-*a-naphthylcarbamidopropionic acid*, $C_{14}H_{14}O_3N_2$, needles, m. p. 198—200° (decomp.), $[\alpha]_D^{20}$ +3·80 in *N*/2-sodium hydroxide; d-*a-naphthylmethylhydantoin*, $C_{14}H_{12}O_2N_2$, m. p. 166°, $[\alpha]_D^{20}$ −17·85° in acetone; *a-carbamidobutyric acid*, $C_5H_{10}O_3N_2$, m. p. 184°. The melting points of the following compounds have been determined, and found to differ from those hitherto recorded: hydantoic acid, 179—180°; *dl*-methylhydantoin, 155—156°; *dl*-a-phenylcarbamidopropionic acid, 174°; *dl*-a-phenylmethylhydantoin, 178°; a-carbamido-a-methylpropionic acid, 184°; *dl*-hydantoinacetic acid, 228—229°, and *dl*-hydantoinpropionic acid, 179—180°.

H. W. B.

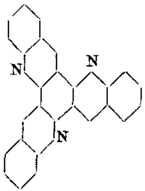
Constitution and Colour. VI. Triphenylmethane Dyes. F. Kehrmann (*Ber.*, 1918, **51**, 468—474).—The constitution of

the various salts of triphenylmethane bases is discussed. Most of the facts are already known, but the theories developed are based also on the results of spectrographic observations which will be published later. The novel feature is the suggestion that the central carbon atom participates in the formation of the highest type of salts, namely, those which only exist in strongly acid solutions. The extra equivalent of acid is attached by residual or main affinities to this atom. For example, the yellow solution of triphenylmethyl chloride in a solution of hydrogen chloride in acetic acid is supposed to contain the salt, $\frac{H}{Cl}\!>\!CPh_2\!:\!C_6H_4\!<\!\frac{H}{Cl}$, and the golden-yellow, tetra-acid salts of magenta are written

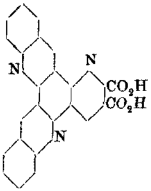


J. C. W.

Oxidative Degradation of Phloroquinyl. I. Pyrquinacridine and its Carboxylic Acids. L. T. BRATZ and ST. VON NIEMENTOWSKI (*Ber.*, 1918, **51**, 366—376).—Phloroquinyl (I) (A., 1906, i, 210) is a remarkably stable substance which can only be oxidised at all readily by means of sodium dichromate in solution in moderately concentrated nitric acid. The product of this reaction is a yellow, crystalline acid, *pyrquinacridinedicarboxylic acid* (II). It is a very sparingly soluble acid, m. p. 375°, which

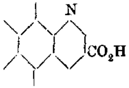


(I.)



(II.)

crystallises from much acetone in almost colourless needles with $1COMe_2$, and from boiling glacial acetic acid in very slender needles with 1AcOH, or golden-yellow prisms with 2AcOH. It dissolves readily in dilute alkali hydroxides or carbonates, ammonia, or boiling sodium acetate solution, the salts being precipitated on adding an excess of the alkaline agent; the *potassium* and *silver* salts are mentioned. Heated with acetic anhydride, the acid changes into its *anhydride*, which crystallises in silky needles, m. p. 374°, whilst treatment with 20% hydrochloric acid at 180—190° results in the formation of *pyrquinacridinecarboxylic*



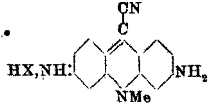
acid (annexed scheme). This is even less soluble than the dicarboxylic acid, but crystallises from nitrobenzene in very slender, curved needles, m. p. 380—382°. The *anilide*, $C_{30}H_{18}ON_4$, is obtained by cautiously heating the dicarboxylic acid with aniline, in yellow needles, m. p. 338°.

The parent substance, *pyrquinacridine*, $C_{23}H_{13}N_3$, is obtained by distilling the acids with lime. It crystallises from toluene in almost colourless, slender needles, m. p. 265°, and dissolves in concentrated acids, salts being deposited on dilution. The following are described: *hydrochloride*, B,2HCl,2·5H_2O; *hydriodides*, B,3HI (possibly, however, B,I_2,HI) and B,HI; *nitrates*, B,3HNO_3 and B,HNO_3. J. C. W.

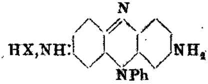
The Simplest Rhoduline. F. KEHRMANN and M. RAMM (*Ber.*, 1918, **51**, 385—388).—An account of the preparation and properties of 3:7-diamino-5-methylphenazonium salts.

3:7-Diacetylaminophenazine is mixed with methyl sulphate (1 mol.) and nitrobenzene at 150°, and the product is treated with hydrochloric acid, whereby a mixture of the chlorides of three methyl derivatives is precipitated. This is repeatedly extracted with hot alcohol, which dissolves small quantities of the chloride of 2:8-diacetylamino-5-methylphenazonium, and the residue is hydrolysed by dissolving in sulphuric acid and cautiously mixing with water. The dark red solution is then rendered alkaline by ammonia and extracted with ether, which dissolves 3-amino-7-methylaminophenazine, when the 3:7-*diamino-5-methylphenazine* remaining in the red solution may be precipitated in the usual way as the *nitrate*, long, metallic-green needles, *perchlorate* (green solution in concentrated sulphuric acid, becoming violet and then red on dilution), *platinichloride*, or *dichromate*. J. C. W.

Phencyazonium Compounds. F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, **51**, 388—391).—Ehrlich and Benda (A., 1913, i, 904) treated some acridine and pyronine dyes with potassium cyanide, thereby obtaining "leucocyanides," which yielded on oxidation dyes with the same properties as the corresponding azonium salts. For example, 2:8-diamino-10-methylacridine yields 2:8-diamino-5-cyano-10-methylacridine salts (I) which resemble phenylsafranine salts (II).



(I.)



(II.)

It appears, therefore, that the :C·C:N group has about the same

tinctorial influence as the nitrogen atom, and it seemed to be o interest to prepare the chromogen of this type.

This is obtained by oxidising Kaufmann and Albertini's 5-cyano 10-methyldihydroacridine (A., 1909, i, 606), a warm acetic aci solution being merely exposed to the air. The 5-cyano-10-methyl acridinium salt, or "10-*methylphencyazonium*" salt, so forme may be converted into the *perchlorate*, which crystallises i yellowish-brown leaflets, and dissolves in sulphuric acid with orange yellow colour, forming a mono-acid salt only. J. C. W.

The Products of the Condensation of 2 : 4-Dichlorophenyl hydrazine with Aldehydes, 1 : 2-, 1 : 3-, and 1 : 4-Diketone and 1 : 3-Ketocarboxylic Esters, and their Behaviou towards Chlorine. CARL BÜLOW [with R. HUSS] (*Ber.*, 1918, **51** 399—417).—The author has shown recently that phenylhydrazone of the type NHPh·N:C(NHR)·CO_2Et are decomposed by chlorin in cold alcohol, the phenylhydrazine residue being removed as diazonium chloride (this vol., i, 42, 196). It appeared to be o interest, therefore, to examine the action of chlorine on simpl phenylhydrazones, NHPh:CHR, and in the sequel it appears tha a diazonium salt is always formed if the compound is a genuin phenylhydrazone. In fact, the non-production of a diazonium sal may be taken as strong presumptive evidence that the so-calle phenylhydrazone has some other structure.

2:4-Dichlorophenylhydrazine was chosen as a base from whicl to prepare suitable hydrazones. It may be obtained by boiling ethyl α-*o*-toluidinoglyoxylate 2:4-dichlorophenylhydrazone wit hydrochloric acid (*ibid.*, 197) or from 2:4-dichloroaniline by th usual method (Chattaway and Pearce, T., 1915, **107**, 32).

The 2:4-*dichlorophenylhydrazone* of *o-chlorobenzaldehyde* $C_6H_4Cl\cdot CH:N\cdot NH\cdot C_6H_3Cl_2$, crystallises in felted, pale yellow needles, m. p. 168—169°, and forms a yellow solution when chlorine is slowly passed into a suspension in cold alcohol. This solution contains a diazonium salt, $C_6H_3Cl_2\cdot N_2Cl$, for it couples with β-naphthol or α-naphthylamine, and it yields a substance, m. p. 82—86°, on treatment with water. m-*Nitrobenzaldehyde*-2:4-*dichlorophenylhydrazone* forms yellow needles, m. p. 207°, and dissolves in cold alcohol when treated with chlorine, the solution almost immediately depositing a substance, m. p. 146—147°, and coupling with β-naphthol to form 2:4-*dichlorobenzeneazo-β-naphthol*, m. p. 188—189°. *Salicylaldehyde*-2:4-*dichlorophenylhydrazone* crystallises in glittering needles, m. p. 148°, and also yields a diazonium salt with chlorine. *Vanillin*-2:4-*dichlorophenylhydrazone*, m. p. 135°, likewise forms the diazonium salt. These hydrazones dissolve in concentrated sulphuric acid with deepening of colour, but are precipitated with the original tints if the solutions are quickly poured on ice.

Benzil yields a compound which is indifferent to chlorine. It can scarcely be, therefore, the normal "osazone," although it has the same composition, and it is probably 5:6-*diphenyl*-2:3-*di-op*-

dichlorophenyl-1 : 2 : 3 : 4-*tetrahydro*-1 : 2 : 3 : 4-*tetrazine*,

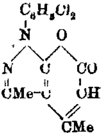
$$C_6H_3Cl_2\cdot N<\begin{matrix}N(C_6H_3Cl_2)\cdot NH\\NH\text{———}CPh\end{matrix}>CPh.$$

It crystallises in lemon-yellow needles, m. p. 217°.

Similarly, benzoylacetone yields 1-op-*dichlorophenyl-5-phenyl-3-methylpyrazole*, $C_6H_3Cl_2\cdot N<\begin{matrix}N{=\!=}CMe\\CPh{:}CH\end{matrix}$ in snow-white needles, m. p. 95°, which is attacked by chlorine, but without producing a diazonium salt.

Ethyl diacetosuccinate gives *ethyl* 1-op-*dichloroanilino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, $C_6H_3Cl_2\cdot NH\cdot N<\begin{matrix}CMe{:}C\cdot CO_2Et\\CMe{:}C\cdot CO_2Et\end{matrix}$, in snow-white needles, m. p. 102°, which dissolves without colour change in sulphuric acid and does not form a diazonium salt.

Ethyl acetoacetate forms "1-op-*dichlorophenyl*-3 : 4-*dimethyl*-1 : 2-*pyrazo*-6 : 7-*pyrone*" (annexed formula), which crystallises in yellow, rhombic leaflets, m. p. 223°. This is very stable towards acids or dilute alkalis, and, whilst chlorine does attack it, no diazonium salt is formed.



Acetone 2 : 4-*dichlorophenylhydrazone* is an unstable substance which crystallises in rhombs, m. p. 42°, b. p. 200°/100 mm., and is condensed by zinc chloride at 190° to 5 : 7-*dichloro-2-methylindole*. This forms large, highly refractive, rhombic crystals, m. p. 61°, and gives a deep violet-red coloration when a very minute trace is moistened with concentrated hydrochloric acid. J. C. W.

Development of Colours Produced on the Plant Fibre with Diazotisable Dyes. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P., 303409, 1917; from *Chem. Zentr.*, 1918, i, 495—496).—The dye, after diazotisation in the usual way, is developed by treatment with an *N*-alkyl derivative of chloro-*m*-phenylenediamine.

4-*Chloro-m*-phenylene-ethyldiamine, colourless crystals, m. p. 53°, can be obtained by nitrating *p*-chloroacetoethylanilide, followed by removal of the acetyl radicle and reduction of the remaining *p*-chloro-*m*-nitroethylaniline. 4-Chloro-*m*-phenylenedimethyldiamine, colourless leaflets, m. p. 80°, is obtainable by nitrating *o*-chlorodimethylaniline and reducing the resultant nitro-compound. D. F. T.

Globulin of Buckwheat, Fagopyrum fagopyrum. CARL O. JOHNS and LEWIS H. CHERNOFF (*J. Biol. Chem.*, 1918, **34**, 439—445).—The globulin of buckwheat has the following percentage composition: C 51·69, H 6·90, N 17·44, S 1·16, and O 22·81. It contains about 13% of arginine, 0·6% of histidine, 7·9% of lysine, and 1% of cystein, besides a small amount of tryptophan. H. W. B.

Stizolobin, the Globulin of the Chinese Velvet Bean, Stizolobium niveum. CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1918, **34**, 429—438).—The new globulin, *stizolobin*, is the chief protein in the Chinese velvet bean. It has the following percentage composition: C 53·03, H 7·05, N 16·33, S 0·65, and O 22·94; and it contains about 1·15% of cystein, 6·7% of arginine, 2·4% of histidine, and 8·5% of lysine. Tryptophan is also present in stizolobin. H. W. B.

The Swelling of Protein Colloids. LAURENCE J. HENDERSON and EDWIN J. COHN (*J. Amer. Chem. Soc.*, 1918, **40**, 857—861).—In reference to the investigations of Fischer and his co-workers (this vol., i, 129, 130, 131), it is stated that careful consideration of the experimental results fails to support the conclusions which have been drawn (see following abstract). D. F. T.

The Colloidal-Chemical Theory of Water Absorption by Protoplasm. MARTIN H. FISCHER (*J. Amer. Chem. Soc.*, 1918, **40**, 862—867).—A reply to Henderson and Cohn (preceding abstract). D. F. T.

Swelling of Protein Colloids. L. J. HENDERSON (*J. Amer. Chem. Soc.*, 1918, **40**, 867—868).—A reply to Fischer (preceding abstract). D. F. T.

Preparation of Strong Solutions of Hæmoglobin and of Colour Filters of Hæmoglobin Compounds. H. HARTRIDGE (*J. Physiol.*, 1917, **51**, 252—258).—Solutions of hæmoglobin containing up to 48% were obtained by dialysing centrifuged sheep's corpuscles in a collodion tube against flowing distilled water at 0° for a week or less in Dewar vessels. By mixing with warm gelatin solutions, colour filters of oxy- and carbonmonoxide-hæmoglobin were prepared, but they were not permanent. G. B.

Hæmin Crystals and their Production. ZDZISLAW ZAWALKIEWICZ (*Pharm. Post.*, 1918, **51**, 45; from *Chem. Zentr.*, 1918, i, 540—541).—Teichmann's reaction is obtained most easily by placing a small quantity of the substance under examination on an objective glass with a drop of *N*/10-hydrochloric acid; this is then very carefully dried above a small flame, the residue moistened with 2—3 drops of concentrated acetic acid and a cover glass placed over the mixture. The mixture is again carefully warmed for about a minute, any acid lost by evaporation being replaced by another drop. When the end of the reaction is indicated by a reddish-brown colour, the remainder of the acid is allowed to evaporate, one or two drops of glycerol are introduced under the cover glass, and the characteristic crystals of hæmatin chloride are examined under the microscope. Ammonium chloride can be used satisfactorily in place of sodium chloride. D. F. T.

Crystalline Nucleic Acids. S. J. THANNHAUSER and G. DORFMÜLLER (*Ber.*, 1918, **51**, 467—468).—Triphosphonucleic acid

(this vol., i, 47) has been partially hydrolysed to *cytidine-phosphoric acid*, $C_9H_{14}O_8N_3P$, rosettes of stout monoclinic-sphenoidal crystals, m. p. 227° (decomp.) (*di-brucine* salt, m. p. 180—182°), and *guanosine-adenosine-phosphoric acid*, $C_{20}H_{28}O_{15}N_{10}P_2$, stout, unsymmetrical triclinic crystals, m. p. 208° (decomp.) (*tetra-brucine* salt, m. p. 170°). Details of the process employed will be given in a subsequent, comprehensive communication.

J. C. W.

Stoicheiometrical Character of the Action of Normal Salts on the Swelling of Gelatin. JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 77—95. Compare this vol., i, 240; and Fenn, this vol., i, 318, 319).—The method previously described for the estimation of the effect of normal salts on the swelling of powdered gelatin has been applied to sodium gelatinate prepared by the action of *M*/100-sodium hydroxide, and to gelatin chloride prepared by the action of *M*/100-hydrochloric acid, on gelatin. It is found that the additional swelling of gelatin chloride is inhibited in solutions of normal salts with univalent cations and anions (type sodium chloride) in concentrations above *M*/64, and by salts with bivalent cations and univalent anions (type calcium chloride) in concentrations exactly half as high, namely, above *M*/128, no matter what the nature of cation or anion. Salts with bivalent anions (type sodium sulphate) have a limiting concentration of a much lower order, namely, *M*/512. In the case of sodium gelatinate, the limiting molecular concentration at which swelling is inhibited is twice as great for salts containing univalent anions and cations (such as sodium chloride) as for salts containing bivalent anions and univalent cations (such as sodium sulphate), whilst salts with bivalent cations (such as calcium chloride) have much lower limiting molecular concentration. Further, the additional swelling of gelatin, treated with *M*/8- or *M*/4-sodium chloride solution, is inhibited by normal salts in exactly the same way and at the same concentrations as sodium gelatinate. The normal salts, therefore, produce the same type of compounds with gelatin as the bases, namely, metal gelatinates which dissociate into a positive metal and a negative gelatin ion. These facts show that the limiting concentration of normal salts for the additional swelling is, within the restrictions mentioned, independent of the nature of the anion and cation of the salt, and this method could be used to calculate roughly the molecular concentration of the salt used.

When normal salts act on sodium gelatinate, apparently only the cation of the salt combines with the gelatin; and when normal salts react with gelatin chloride, only the anion will combine with gelatin, but not the cation. The experiments also show that gelatin salts with univalent anion or cation, such as gelatin chloride or sodium gelatinate, are capable of additional swelling, whilst salts of gelatin with bivalent ions are not. It is suggested that the swelling is due to electrolytic dissociation, which only occurs to a small extent in the case of gelatin salts with bivalent ions. It is evident that antagonistic salt action may be expected when

gelatin salts containing univalent ions are transformed into gelatin salts with bivalent ions. H. W. B.

Influence of Normal Salts on the Viscosity of Gelatin Solutions. JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 395—413. Compare preceding abstract).—After gelatin has been treated with *M*/8- or *M*/16-solutions of normal salts with univalent cations, and the excess of salt then washed away, its viscosity is found to have increased. The viscosity is estimated by dissolving an amount of the treated gelatin, corresponding with 1 gram of the dry material, in water and comparing the rate of outflow through a viscometer at 24° with that of a solution containing 1 gram of washed gelatin powder in the same volume (100 c.c.) of water. The effect on the viscosity is stoicheiometrical, in so far that all normal salts with univalent cations produce the same increase in the viscosity of the gelatin solution, so long as the concentration of cation is the same, regardless of the nature and valency of the anion. Salts with bivalent cations do not produce any increase in the viscosity of gelatin.

The action of salts on the viscosity of sodium gelatinate is similar to that observed in the case of gelatin, but with gelatin chloride (gelatin previously treated with *N*/100-hydrochloric acid) salts with bivalent anions lower the viscosity of such treated gelatin, salts with univalent anions have the opposite effect, whilst the influence of the cations is imperceptible.

These results indicate that the viscosity of a gelatin solution is influenced chiefly, if not exclusively, by only one of the two ions of the normal salt, namely, the one with an electrical charge opposite to that of the protein. Ordinary gelatin has acidic properties, and its viscosity is influenced, therefore, only by cations. The same position is occupied by sodium gelatinate, but gelatin chloride, yielding a positive gelatin ion, is affected only by anions. Support is also afforded by these results to the hypothesis that gelatinates with univalent cations are highly dissociable, whilst those with bivalent cations are not. H. W. B.

Effects of Electrolysis on Gelatin and their Biological Significance. III. Effects of Mixtures of Salts on the Precipitation of Gelatin by Alcohol. Antagonism. W. O. FENN (*J. Biol. Chem.*, 1918, **34**, 141—160. Compare this vol., i, 240; and Loeb, preceding abstract).—By the method previously described, it is shown that salts (like sodium chloride) with univalent anions and cations decrease the effect of salts with bi- or ter-valent anions or cations on the precipitability of gelatin by alcohol, whilst salts with bi- or ter-valent cations antagonise those with bi- or ter-valent anions. Small concentrations of salts with bivalent cations (like calcium chloride) decrease the effect of sodium chloride on gelatin, whilst small concentrations of salts with bi- or ter-valent anions (like sodium sulphate) increase it. A pair of salts with bivalent cations or a pair with univalent anions and cations are not antagonistic in their effects. H. W. B.

Effects of Electrolytes on Gelatin and their Biological Significance. IV. Precipitation of Gelatin by Mixtures of Salts. W. O. FENN (*J. Biol. Chem.*, 1918, **34**, 415—428. Compare preceding abstracts).—The effect of a mixture of salts on the precipitability of gelatin depends on the nature of the ions which are present. The experiments are performed by dissolving the gelatin in acid, alkali, or a normal salt, and estimating the amount of sodium chloride or sulphate which must be added in the solid form just to cause its precipitation. Acids, and salts in which the effect of the cation predominates, assist the precipitation of gelatin by sodium chloride, whilst alkalis, and salts with predominant anions, hinder it. When sodium sulphate is substituted for sodium chloride, the precipitation of the gelatin is hindered by small, and assisted by higher, concentrations of alkali. H. W. B.

The Variability in the Activity of Ptyalin. F. DE BRUYNE (*Arch. néerland. physiol.*, 1918, **2**, 358—363).—Some observations indicating a periodicity in the activity of ptyalin when kept at 35°. S. B. S.

Physiological Chemistry.

Respiratory Metabolism and the Question as to the Formation of Sugar from Proteins and their Degradation Products. JOSÉ M. DE CORRAL (*Biochem. Zeitsch.*, 1918, **86**, 176—222).—It has been shown that the administration of Witte's peptone to a dog renders the liver practically free from glycogen. The effect of this administration on the respiratory quotient has been investigated, and also the effect of adding protein and amino-acid diets after peptone treatment. The Jacquet apparatus was employed for measurement of the gaseous exchanges. After eight days' starvation, the respiratory quotient for dogs sinks to 0·682, which is less than that after ingestion of fat. Practically the same low respiratory quotient is obtained after an interval of some hours after the last treatment, when the animal has had Witte's peptone administered to it for two days. When a carbohydrate diet is given, it is possible to determine the formation of glycogen by ascertaining the respiratory quotient seventeen or eighteen hours after the last ingestion. That the capacity for forming glycogen from carbohydrates after administration of peptone is diminished can be ascertained, even after an interval of twenty-four hours. But although diminished, it still exists, as is shown by comparing the value of the respiratory quotient with that obtained after administration of carbohydrates during starvation. If fats exclusively are administered after two days' treatment with peptone, the respiratory quotient in a following period

of starvation is the same as that after peptone action. If, after peptone treatment, amino-acids or proteins are administered, carbohydrates are formed, for the respiratory quotient in the following period of starvation indicates combustion of carbohydrates. Such a formation of carbohydrates from amino-acids or meat only appears to take place, however, when carbohydrates are wanting in the organism. S. B. S.

The Wanderings of the Ions in Serum and Blood under the Influence of Carbon Dioxide, Acid, and Alkali. H. J. HAMBURGER (*Biochem. Zeitsch.*, 1918, **86**, 309—324).—The author, using an ultra-filtration method, is able to confirm the statement of Rona and György, that when carbon dioxide acts on the serum, the chlorine passes into a non-diffusible form, by combining with the proteins. The same happens after addition to the serum of very small amounts of sulphuric acid and of larger amounts of acetic acid. SO_4 also passes into a non-diffusible form after treatment of the serum with hydrochloric acid. When carbon dioxide acts on blood, it is possible to ascertain that not only does SO_4 attach itself in non-diffusible form to the serum proteins, but that it also goes into the corpuscles. The same phenomena take place after addition to blood of minute amounts of hydrochloric acid. The reverse effect to that produced by acids is observed after addition of small amounts of potassium hydroxide, in that Cl and SO_4 are set free from combination with the proteins and pass into a diffusible form. S. B. S.

Can the Amount of Combination of Carbon Dioxide with Blood-serum be regarded as a Measure of the Reaction of the Blood? K. A. HASSELBALCH and E. J. WARBURG (*Biochem. Zeitsch.*, 1918, **86**, 410—420).—The carbon dioxide tension, under which the blood is centrifuged for separation of the serum, is of great influence. By high carbon dioxide tension during centrifugalisation, the curve representing the relationship between carbon dioxide tension and carbon dioxide bound to the serum is shifted upwards, whereas by lower tension during centrifugalisation, it is shifted downwards. For this reason, it is not possible to draw correct conclusions as to acidosis and the reaction of the blood by measuring the capacity of the serum to combine with carbon dioxide, unless account is taken of the tension of the carbon dioxide prevailing during the preparation of the serum from the blood. It may be recalled that the carbon dioxide tension influences also the distribution of Cl' and other ions between the serum and corpuscles (Hamburger). S. B. S.

The Presence of Phosphates in Human Blood-serum. V. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **86**, 395—409. Compare A., 1917, i, 520; this vol., i, 50, 203).—An analysis of the various forms of phosphorus in the serum in six pathological cases. S. B. S.

The Presence of Invertase in Serum. G. H. Boissevain (*Arch. néerland. physiol.*, 1918, **2**, 415—419).—The discordant results of various observers as regards the presence of invertase in the serum after injection of sucrose are discussed. It is shown that the leucocytes contain invertase, and it is suggested that the presence in the serum after injection of various sugars in solution is due to the injury of the leucocytes and the setting free of the ferment; in fact, an invertase can be detected in the serum after injection of water, or the formation of a clot in the veins by introduction of a silk thread. The leucocytes used in the experiments were obtained from an aseptic abscess produced by terebenthene. S. B. S.

Antigens. XII. The Relationship between Serological Specificity and Chemical Structure. (Preparation of Antigens with Specific Groups of known Chemical Structures). Karl Landsteiner and Hans Lampl (*Biochem. Zeitsch.*, 1918, **86**, 343—394).—A series of antigens was made by combining horse serum with the diazo-derivatives obtained from the following "azo-components": aniline, *o*-, *m*-, and *p*-aminobenzoic acids, *o*-, *m*-, and *p*-aminobenzenesulphonic acids, *p*-aminophenylarsinic acid, and a number of chloro-, bromo-, and nitro-*o*-substitution products of these substances, *o*-, *m*-, and *p*-aminocinnamic acids, naphthionic acid, and aminoazobenzenedisulphonic acid. The method of preparing solutions containing serum proteins coupled with these various diazo-derivatives is described. The antigens were then injected into rabbits until active immune sera were obtained. The precipitin reaction of the various immune sera towards native horse sera differed. The reaction of the immune sera towards the various antigens (diazo-proteins) prepared from horse serum, egg-albumin, and in a few cases edestin, was also investigated. Altogether 23 kinds of immune sera were prepared, and their action on 33 azoproteins was investigated. Of these, only 6 were completely specific, acting only on the homologous antigens containing the same azo-components. Of the antigens, 15 acted only with one immune serum. The other immune sera and antigens showed a broader sphere of action. The results are tabulated by the author, who summarises the relationship of the various antigens to one another and the relationship of the chemical structure of the azo-components and serological action. The possibility of distinguishing chemical groups by serological reactions is suggested. S. B. S.

Calcium and Magnesium Metabolism. IV. Experiments on Man. Maurice H. Givens (*J. Biol. Chem.*, 1918, **34**, 119—130. Compare A., 1917, i, 603).—The daily urinary excretion of calcium and magnesium of nine healthy adults on a diet of natural foods containing more magnesium than calcium, ranged from 0·05 to 0·24 gram of calcium and from 0·03 to 0·15 gram of magnesium whilst on a diet having more calcium than magnesium the limits

were 0·12 to 0·47 gram of calcium and 0·05 to 0·23 gram of magnesium. In general, although not always, more calcium than magnesium is excreted in the urine. The urinary output of both calcium and magnesium is increased by consumption of milk; calcium lactate always increases the urinary excretion of calcium, although not to such an extent as is effected by milk; magnesium lactate does not seem to produce any greater elimination of magnesium in the urine. The results obtained do not allow of any simple relationship being established between urinary excretion of calcium and body-weight. H. W. B.

Carbohydrate Metabolism. I. Elimination of Sugar in the Urine of the Normal Dog. STANLEY R. BENEDICT and EMIL OSTERBERG [with CECIL DUDLEY] (*J. Biol. Chem.*, 1918, **34**, 209—216).—By means of a new method for estimating traces of sugar in urine (this vol., ii, 247), the authors are able to record the changes in the hourly excretion of sugar by a normal dog. The amount of sugar eliminated is independent of the volume of urine secreted. The percentage of sugar varies greatly; in one dog it ranged from 0·021 to 0·36%. The amount of sugar excreted per hour gradually rises after a meal, reaches a maximum in about five hours, and then falls to normal. The urine almost invariably contains some kind of sugar, but occasionally during the periods of minimum elimination, fermentable sugar (dextrose) disappears entirely from the urine. During the period of maximum sugar elimination, the reaction of the urine approaches neutrality, and in some cases becomes alkaline to litmus. The twenty-four hours' sample was invariably acid. The discussion of the bearing of these points on views as to carbohydrate metabolism is reserved for a future paper. H. W. B.

Carbohydrate Metabolism. II. Urinary Sugar Excretion in Two Normal Men. STANLEY R. BENEDICT, EMIL OSTERBERG, and ISAAC NEUWIRTH (*J. Biol. Chem.*, 1918, **34**, 217—262. Compare preceding abstract).—The results show that sugar is always present in normal human urine. Feeding with either meat or a carbohydrate diet causes an increase in the elimination of sugar. Glycosuria is therefore a physiological condition, and the normal organism can be said to be diabetic. The authors propose to abandon the use of the word "glycosuria," and suggest the term "glycuresis" to denote an increase of sugar in the urine. Glycuresis occurs after the ingestion of food, the percentage of sugar in the urine rising after a meal from about 0·05 to 0·3 or sometimes to as much as 0·6. A certain degree of tolerance for dextrose is shown in that, after the ingestion of 20 to 50 grams of dextrose, the resulting glycuresis is not greater than is observed after an ordinary meal. Yet the addition of 20 grams of dextrose to an ordinary meal may lead to a relatively great output of sugar in the urine, indicating a profound disturbance in carbohydrate metabolism. The total amount of sugar eliminated in the urine by a normal person is about 1 to 1·5 grams daily, and in persons

with a tendency to diabetes this maximum is not only exceeded, but the ratio of unfermentable to fermentable sugar in the urine becomes changed. H. W. B.

Inorganic Elements in Nutrition. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 131—140).—Full description of work previously published (this vol., i, 277). H. W. B.

Nutritive Factors in Animal Tissues. II. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 17—27. Compare this vol., i, 140).—Besides the liver, the heart, kidney, or brain of the pig contains sufficient water-soluble vitamine to effect rapid growth in the rat when constituting the sole source of protein and water-soluble vitamine in the food. In some cases, normal growth occurs also without the addition of any source of fat-soluble vitamine other than that contained in the tissue itself. These tissues are therefore better foods than dried beef (compare Cooper, A., 1914, i, 777, and Osborne and Mendel, *loc. cit.*). They can be dried and heated for several hours at 90° without any loss of water-soluble vitamine occurring. The oil expressed from liver tissue is rich in fat-soluble vitamine, and it effectively cures or prevents the nutritive decline and the pathological manifestations which are the characteristic outcome of feeding with a diet otherwise devoid of fat-soluble vitamine. H. W. B.

The Nature of the Constituent of Intestinal Extracts which Exerts a Stimulating Influence on the Gastro-intestinal Movements. J. W. LE HEUX (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 805—811).—The presence of this constituent was first demonstrated by Wieland. The author describes experiments for its isolation, and draws the conclusion that it is most probably choline. Its physiological activity is markedly increased by acetylation. S. B. S.

Quantity of Metal Fixed by Organic Extracts and Proteins. II. Catalytic Power of Egg-albumin treated with Metallic Powders. S. REBELLO-ALVES and A. BENEDICENTI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 79—96, 150—156; from *Physiol. Abstr.*, 1918, **3**, 100).—Powdered copper and cobalt are fixed in varying proportions by different organs; liver, owing to its more rapid autolysis, fixes most.

The catalytic power of egg-albumin towards hydrogen peroxide is not increased by heating it with powered quartz, but is increased five or six times by cobalt powder. Nickel, iron, and copper do not increase catalysis, and lead and antimony diminish it. S. B. S.

Suprarenal Glands in Relation to Carbohydrate Metabolism. I. Influence of Repetition of Adrenaline Injection on the Intensity of Glycosuria and Hyperglycæmia and the Glycogen Content of the Liver. II. Influence of Adrenalectomy on the Glycogenetic Power of the Liver. III. Adrenaline Content of the Suprarenal Glands in Various Experimental Conditions. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **34**, 269—285, 287—297, 299—319).—Daily repetition of subcutaneous injection of adrenaline is followed on each occasion by the excretion of about the same quantity of sugar in the urine so long as the animals (rabbits) are well fed. When the animals are allowed to fast, the daily sugar excretion rapidly diminishes until only a slight glycosuria is produced. The hyperglycæmia produced by daily adrenaline injections remains practically constant, no matter whether the animal is fasting or well fed. The reason of the failure of the hyperglycæmia caused by the injection of adrenaline into fasting animals to produce the typical glycosuria is not elucidated. Injection of adrenaline into fasting rabbits leads to a storage of glycogen in the liver. A combination of fasting and adrenaline injections does not therefore render the liver of an animal free from glycogen.

Rats after adrenalectomy still retain the power to form glycogen from carbohydrates in the liver; adrenaline does not exert a controlling action on the glycogenetic function of the liver.

The amount of adrenaline in the suprarenal gland after removal from the body gradually diminishes unless the gland is kept in an oxygen-free medium. The adrenaline content of the gland in the living rabbit is not altered by fasting, by repeated injections of adrenaline, or by injection of a single large dose of this substance. Removal of one gland is partly compensated for by growth of the companion gland, resulting in an increase in the absolute amount of adrenaline in the gland, although, owing to the relatively greater growth of the glandular tissue, the percentage of adrenaline in the companion gland is reduced. H. W. B.

Estimation of Various Forms of Nitrogen in Raw Beef, including the Products of Hydrolysis of some of the Proteins. I. Hexone Bases of some Proteins of Beef. II. Bromination of the Hydrolysates of some Proteins of Beef. WALTER E. THRUN and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1918, **34**, 343—353, 355—362. Compare Trowbridge and Grindley, A., 1906, ii, 374).—The proteins of beef which are insoluble in cold water, yield on hydrolysis less humin, ammonia, histidine, and more arginine nitrogen than the coagulated water-soluble proteins. Since the former represent the stroma and the latter the plasma of the muscle fibres, it appears that these components of the cell are composed of essentially different proteins. The comparison of the analyses of the muscular tissues of a new-born calf and of a five-year-old steer indicates that during growth the insoluble proteins probably change in composition.

A method is described for estimating histidine in proteins by

hydrolysis followed by bromination. After deducting the amount of bromine absorbed by cysteine and allowing for the solubility of histidine in phosphotungstic acid, figures are obtained which tally closely with those afforded by Van Slyke's method (A., 1911, ii, 944). Under the conditions described, a molecule of cysteine absorbs about ten atoms of bromine, whilst a molecule of histidine absorbs two. H. W. B.

The Skin Secretion of Frogs. FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1917, **81**, 319—382).—The secretion is best obtained by electrical stimulation of washed frogs, and consists of coagulable protein, mucin, albumoses, peptones, amino-acids (7% of leucine), purine bases, cholesterol and its esters. The dried secretion kills tadpoles and small fishes in a 1:80,000 solution; 6—12 mg. per kilo. intravenously kills rabbits. The dried secretion has a strong local irritant action on the skin; the active substance resembles the saponins in its chemical and pharmacological properties, and is quite distinct from the heart poison of the toad's skin. It could not be obtained pure, but gives Liebermann's cholesterol reaction and seems to be a lactone. G. B.

The Excretion of Saponins in the Urine, and their Action on the Blood after Internal Administration. JOSEF FIEGER (*Biochem. Zeitsch.*, 1918, **86**, 244—297).—Sapindus saponin, after administration to dogs, is partly excreted in the unchanged form in the urine, and can be detected by its hæmolytic action. The sapogenin can also be isolated from the urine after hydrolysis with sulphuric acid; this substance exerts also a hæmolytic action. The detection of the guaiacum saponin in the urine is most difficult, as it is not hæmolytic. The author shows, however, that it yields on hydrolysis two sapogenins, the mixture of which is strongly hæmolytic. The urine of an animal to which the saponin had been administered is not hæmolytic, but it exerts a hæmolytic action after hydrolysis. The saponin is therefore excreted in the urine unchanged. In an experiment with quillaja saponin, this substance could not be detected in the urine; in this case, however, the experiment had been carried out on an animal to which other saponins had been previously administered, and reasons are given for supposing the animal had acquired a general tolerance to the group of saponins, and had degraded the quillaja saponin in the intestine, excreting the sapogenin in the fæces. In the case of a second dog to which the saponin was administered, small amounts were found in the urine. In the case of all three saponins, a marked excretion of bile pigments in the blood took place, which is taken as evidence of the resorption of these substances. They also exerted a temporary diuretic action. S. B. S.

The Excretion of Saponin in the Fæces. HANS BÄCK (*Biochem. Zeitsch.*, 1918, **86**, 223—242).—Sapindus and quillaja saponins were administered to hens and dogs. They cause irritation of the alimentary tract, and undergo hydrolysis either by

enzymes or by microbes. The sapogenins are excreted with the fæces, and their presence was detected by their hæmolytic action on the corpuscles of various species. From the sapindus saponin apparently two sapogenins are obtained in the fæces, one of which is soluble in ethyl acetate and is strongly hæmolytic, whilst the other is insoluble and not hæmolytic. From quillaja saponin, two sapogenins also appear to be formed, one soluble in ethyl acetate and strongly hæmolytic, the other insoluble in this reagent, but weakly hæmolytic. S. B. S.

Cæsium Ions and Cardiac Action. H. Zwaardemaker (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 773—778).—The light radioactive metals and the allied cæsium, as well as the heavy radioactive metals uranium, thorium, niton, and radium, sustain the contractility of the isolated frog's heart when the ventricle is pulsating on its own activity. The author gives the effectual doses of these for summer frogs. There is a biological antagonism between potassium, cæsium, and rubidium, on the one hand, and uranium, thorium emanation, and niton, on the other. Probably cæsium emits β-rays of low penetrating power on which its effect, similar to that of potassium and rubidium, depends. S. B. S.

Distribution and Elimination of Zinc and Tin in the Body. William Salant, J. B. Rieger, and E. L. P. Treuthardt (*J. Biol. Chem.*, 1918, **34**, 463—470).—After the administration of zinc salts to cats or rabbits by the mouth, or by subcutaneous or intravenous injections, the metal is eliminated almost entirely in the fæces. Tin salts are similarly dealt with, except that a significant proportion passes off in the urine. Storage of both metals occurs in the liver, skin, and bones. H. W. B.

Production of Glycosuria by Zinc Salts. William Salant and Louis Elsberg Wise (*J. Biol. Chem.*, 1918, **34**, 447—462).—The intravenous injection of zinc malate into rabbits produces slight hyperglycæmia and glycosuria. Glycosuria is also caused by subcutaneous injections and by the administration of the zinc malate or acetate with the food, but much larger doses are required. The amount of sugar in the urine after the injection usually reaches about 0·35 per cent. Albuminuria accompanies the glycosuria and is sometimes very marked. H. W. B.

Dichloroethylene as a Narcotic. Hermann Wittgenstein (*Arch. exp. Path. Pharm.*, 1918, **83**, 235—247).—An atmosphere containing about 1% by volume of dichloroethylene causes deep narcosis in various mammals, but, unlike chloroform, it does not depress the heart and blood vessels. It has been successfully tried on man in a few cases. G. B.

The Taking up of Ethyl Alcohol by the Lungs. A. Loewy and R. von der Heide (*Biochem. Zeitsch.*, 1918, **86**, 125—175).—A detailed investigation of the amounts of ethyl alcohol taken up

from the air by rats and guinea-pigs and of the amounts remaining in the bodies and burnt. As compared with methyl alcohol, the amounts of ethyl alcohol stored in the body are small. The amount stored per millimetre tension of alcohol vapour in the air is smaller the greater the tension. The combustion of ethyl alcohol is greater than that of methyl alcohol, and this accounts for the greater quantities of the latter found stored in the body. The conclusion is drawn that ethyl alcohol is, generally, more toxic than methyl alcohol. A few experiments on man are also described.

S. B. S.

Gossypol, the Toxic Substance in Cotton Seed. W. A. WITHERS and FRANK E. CARRUTH (*J. Agric. Research*, 1918, **12**, 83—102. Compare Carruth, this vol., i, 266).—Cotton-seed meal is much less toxic than raw cotton seed, probably owing to the oxidation of gossypol during cooking. Feeding experiments with rats, rabbits, and pigs are described, details of which are given in *J. Soc. Chem. Ind.*, 1918, 164A. W. G.

Metabolic Changes Induced by Administration of Guanidine Bases. II. Influence of Guanidine on Urinary Ammonia and Acid Excretion. III. Relation between the Tetanoid Symptoms of Guanidine Administration and the Condition of Acidosis. IV. Influence of the Administration of Calcium on the Sugar Content of the Blood in Rabbits with Guanidine Hypoglycæmia. C. K. WATANABE (*J. Biol. Chem.*, 1918, **34**, 51—63, 65—72, 73—76. Compare this vol., i, 205).—The subcutaneous injection of guanidine hydrochloride into a rabbit is followed immediately by a diminished excretion of nitrogen in the urine. The ammonia eliminated in the urine is increased, however, so that the ratio, ammonia/total nitrogen, is greatly increased. There is a fall in the hydrogen ion concentration, and the urine may become neutral or alkaline.

The effect of the injection on the blood is to produce a marked increase in its hydrogen ion concentration and a corresponding decrease in the alkaline reserve, specially noticeable after the manifestation of the symptoms of tetany. It appears, therefore, that the excretion of the excess of ammonia in the urine in tetany is the result of the operation of a protective mechanism by means of which the liver seeks to neutralise the acid produced by the excessive muscular activity (compare Carlson and Jacobson, A., 1910, ii, 324).

All the toxic symptoms following parathyroidectomy are paralleled by those produced by the injection of guanidine into the system. The hypoglycæmia manifested after thyreoparathyroidectomy is also produced by the administration of guanidine (*loc. cit.*), but it is now shown that neither the tetany nor the hypoglycæmia resulting from guanidine injections can be removed by treatment with calcium lactate, which has been shown to abolish these symptoms when produced by operative procedures (compare Underhill and Blatherwick, A., 1914, i, 1184). H. W. B.

The Fate of Quinine in the Organism. HEINZ HARTMANN and LOBO ZILA (*Arch. exp. Path. Pharm.*, 1918, **83**, 221—234).—A gravimetric method of estimation in urine is described (precipitation as tannate, decomposition of the latter, extraction from water with ether), and a method, based on the fluorescence, for estimation in blood (compare Ramsden and Lipkin, this vol., ii, 251). At most, 40% of administered quinine is excreted in urine and fæces; the rest is not deposited in the organs, and must therefore have been destroyed. After intravenous injection, the amount in the blood sinks rapidly, then more slowly, to zero (eight hours after 0·5 gram), but oral administration gives a lower, more constant quinine level, which is retained for about twenty-four hours. G. B.

Physiological Behaviour of Raffinose. II. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **34**, 321—333. Compare Kuriyama and Mendel, A., 1917, i, 611).—Raffinase is present in mung bean (*Phaseolus aureus*), cotton seed, and soja bean. It can also be extracted from rabbits' fæces. Raffinase (from yeast) is readily destroyed by the gastric juice, but when yeast is fed to an animal, a portion of the raffinase escapes destruction and passes into the excreta. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. VI. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **86**, 329—336. Compare A., 1917, i, 305, 430, 528).—Leucine promotes the urease fermentation in the case of *Bacillus coli*, but it inhibits the sugar-fermenting action of the same bacterium. The significance of certain fragments of the protein molecule for the formation of ferments, and the general physiological significance of proteins for growth, are discussed by the author. S. B. S.

Influence of Nitrates on Nitrogen-assimilating Bacteria. T. L. HILLS (*J. Agric. Research*, 1918, **12**, 183—230).—A great increase in the number of azotobacter in sterilised soil was produced by the application of small quantities (up to 0·1%) of potassium, sodium, or calcium nitrate, but ammonium nitrate was much less effective, and higher concentrations of all the nitrates were not so favourable to the growth of the organism. There was also an increase in the total nitrogen in the soil, but this increase was not commensurate with the increase in the number of azotobacter present. On agar films, the results were somewhat different, calcium nitrate causing a decrease in the amount of nitrogen fixed.

All three nitrates caused an increase in the number and size of the volutin bodies in the azotobacter cells and a marked pigmentation. The number of *Bacillus radicicola* in sterilised soil was increased by the application of small quantities of the three nitrates, and, although this increase was less marked than in the case of azotobacter, the *B. radicicola* appeared to be more resistant to higher nitrate concentrations. Unlike the azotobacter, *B. radicicola* does not reduce nitrate to nitrite under aerobic conditions. The presence of large amounts of potassium, sodium, and calcium nitrates proved detrimental to the formation of nodules on alfalfa.

W. G.

Presence of a Growth-producing Substance in Cultures of Typhoid Bacilli. AUGUST J. P. PACINI and DOROTHY WRIGHT RUSSELL (*J. Biol. Chem.*, 1918, **34**, 43—49).—It has long been recognised that in certain infectious diseases growth is induced, apparently, by the infection. In typhoid fever, for example, the patient may grow from one to even several inches in height. It is now shown that the fat- and protein-free extract of typhoid bacilli contains a vitamine which when added to the food causes rapid growth of rats on a diet on which otherwise they gradually lose weight and die. The extract gives the blue coloration with Folin's uric acid reagent, which is given by vitamine-containing extracts prepared from yeast and other sources. The authors indicate the bearing of these results on the question of a more scientific method of feeding in these cases. H. W. B.

The Preparation of Phosphoric Acid Esters of Carbohydrates (Zymophosphate) by Living Yeasts. HANS EULER (*Biochem. Zeitsch.*, 1918, **86**, 337—342).—Neuberg has found that yeast in presence of toluene could only bring about an esterification of 7—8% of added phosphate, whereas the author found that it could bring about a complete conversion into the ester. Attention is now directed to the facts (*a*) that excess of toluene acts toxically and inhibits the zymophosphate formation, although small amounts are necessary to bring this about, and (*b*) not all yeasts are capable of zymophosphate formation; two out of eleven bottom beer yeasts investigated by the author gave negative results. The author confirms Harden and Young in showing that dihydroxyacetone can only give rise to a small amount of zymophosphate. S. B. S.

The Influence which the Plant Function of Yeast Exercises on the Yield of Alcohol; new Interpretation of Ferment Power. L. LINDET (*Compt. rend.*, 1918, **166**, 910—913).—An examination of the relative effects of the plant function and the zymase function of yeast during alcoholic fermentation. The author has studied the effect of varying the nutritive value of the bouillon, the concentration of the sugar solution, the vigour of the yeast, the temperature, the thickness of sowing, and the origin of the yeast on the yield of alcohol. The ferment power

must be considered as the sum of the plant power, tending to consumption of sugar, and the zymase power producing the alcohol. These two powers are higher as the crop of yeast is less abundant and the fermentation is prolonged. Except in the case of temperature variation, the weight of sugar utilised to produce a given weight of yeast is independent of the conditions. [See, further, *J. Soc. Chem. Ind.*, July.] W. G.

Precipitation of Proteins by Narcotics. OTTO MEYERHOF (*Biochem. Zeitsch.*, 1918, **86**, 325—328).—Freundlich and Rona (A., 1917, ii, 365) have explained the sensitisation of colloids to precipitating salts by the action of narcotics. The same explanation applies to the following phenomena, observed with Lebedev's maceration juice of yeast. The original juice is readily precipitated on addition of 6% ethyl urethane. The residue from ultra-filtration is not so precipitated, but precipitation readily takes place when the ultra-filtrate is added to it. The combined action of salts and narcotics is necessary for precipitation. S. B. S.

Growth of Aspergillus glaucus under the influence of Large Quantities of Potassium Nitrate. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 599—602).—A series of tables indicating the marked influence exerted by potassium nitrate on the rapidity of growth of *Aspergillus glaucus*. A. J. W.

Acids Produced by Mucor Boulard. BETTINGER and DELAVALLE (*Bull. Assoc. Chim. Sucr. Dest.*, 1917, **35**, 13—15. Compare *J. Soc. Chem. Ind.*, 1918, 219A, 345A).—*Mucor Boulard* (employed industrially for the saccharification of distillery mashes), cultivated in sugared extract of malt-combs, yields succinic acid as sole non-volatile acid, and a much smaller proportion of acetic acid. The production of acid is favoured by aeration, high sugar-content of the medium, and relatively low temperatures of culture. Ether extracts about 21% of the dry substance of the plant grown under these conditions. J. H. L.

The Formation of Soluble Starch by Moulds and the Question of the Synthesis of Proteins by these Organisms. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1918, **86**, 110—124).—In continuation of his investigations on the formation of soluble starch (A., 1917, i, 370, 503), the author now shows that quinic acid can serve as a source of carbon. In presence of asparagine, the percentage of the acid must be more than 6%, but in the presence of ammonium sulphate, 3·6% of quinic acid is sufficient, as acid is necessary for the process, and in the latter case it is set free from the ammonium sulphate. The author criticises some earlier work dealing with the utilisation of various nitrogenous substances by plants, especially that of Czapek, Brenner, and Puriewitsch. He shows that certain factors have been left out of account in drawing conclusions from experimental results. More especially, he shows

that the acidity of the medium is to be taken into account, which may be due to the acid derived from the salts. His own experiments on the formation of soluble starch require the presence of acid. Furthermore, in estimating the yield of the moulds, no account has been taken of proteoclastic action, in that a mould may grow, and after a time the amount will diminish owing to this action. This factor again is influenced by the presence of acids. S. B. S.

Basis of Measurement of Antagonism. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **34**, 363—368).—A theoretical paper in which the possible methods of measuring the antagonistic action of salts on the growth of plants and animals is discussed. H. W. B.

The Relation of some of the Rarer Elements in Soils and Plants. W. O. ROBINSON, L. A. STEINKOENIG, and C. F. MILLER (*U.S. Dept. Agr., Bull.*, 1917, No. 600; from *Physiol. Abstr.*, 1918, **3**, 75).—About fifty samples of legumes, grasses, vegetables, trees, and shrubs grown on nine soils of known composition, or obtained from localities where certain rare elements were known to occur, were examined. Lithium was found in spectroscopic traces in all the plants examined (max. 0·00015%). Rubidium was found in most cases and in larger quantities than the other rare alkalis (max. 0·025%), and in the cases where the amount of rubidium oxide exceeded 0·01% in the plant, minerals containing this element were known to occur in the soil. Cæsium was found in only three plants obtained from a locality where cæsium beryls occur. Chromium was occasionally found, although always in small quantities. Vanadium was only detected in six cases, and then in traces. Molybdenum was not found. Barium was found in all samples and strontium in all but one, and titanium occurred in minute quantities in all samples. With two exceptions, all the plants contained aluminium, the percentage in pine needles being exceptionally high (max. 0·253%). Methods of analysis are given in an appendix. W. G.

Flavone Derivatives in Plants. III. Tropical Plants. K. SHIBATA and I. NAGAI (*Bot. Mag., Tokyo*, 1916, **30**, 149—178; from *Physiol. Abstr.*, 1918, **3**, 68—69).—The leaves, sprouts, blossoms, bark, and wood of two hundred and forty-two species were examined, and it was found that flavones were invariably present. The flavone glucosides of the cell sap exert a protective action against the solar rays, especially those of short wave-length. Thus plants grown under glass for some time contained less flavone than those grown in the open, and those grown in the shade less than those grown in the sun. Plants provided with a heavy cuticular layer were usually poor in flavones. The function of the flavone in the cell sap of the plants is similar to that of the pigment of the human skin. Flavone and anthocyanin often inter-

change. Thus young sprouts frequently contain anthocyanin-red, which changes into the colourless flavone glucoside in the grown organ, and back again into anthocyanin before the fall of the leaves. The winter buds of many plants contain flavones both in the tissues of the lower leaves and the viscous exudate. In many cases, the wax-like or powdery covering of the plant organs contains flavone compounds secreted by the epidermis [compare Müller, T., 1915, **107**, 872]. W. G.

Some Constituents of the American Grapefruit (Citrus decumana). HARPER F. ZOLLER (*J. Ind. Eng. Chem.*, 1918, **10**, 364—374).—Analyses of grapefruit showed that the peel contained 2·5 to 6·0 grams per fruit of essential oils, principally *d*-limonene (90—92%), with small quantities of citral, α-pinene, geraniol, and linalool; also about 0·2 to 1·6 grams of the glucoside naringin per fruit and about 4 grams of pectin. The pulp contains about 1·9 to 6·0 grams of citric acid, 6·2 to 15 grams of sucrose, and 8·6 to 19·6 grams of dextrose per fruit. [See, further, *J. Soc. Chem. Ind.*, 387A.] W. F. F.

A New Compound in Hyssop Killed by Fungus. O. TUNMANN (*Pharm. Post*, 1917, **50**, 773—774; from *Chem. Zentr.*, 1918, i, 29—30).—The cells of some hyssop plants which had been killed by moulds were found to contain as the chief crystalline deposit a colourless substance which has m. p. 275°, yields protocatechuic acid on fusion with potassium hydroxide, and is probably a flavone derivative. It is designated *hyssopin*, and resembles, but is not identical with, hesperidin, which has already been found in unusually large quantity in mint killed by fungus. J. C. W.

Non-protein Nitrogen of Wheat Flour. M. J. BLISH (*J. Biol. Chem.*, 1918, **33**, 551—559).—The proteins are precipitated from an aqueous extract of wheat flour by treatment first with *N*/10-sodium hydroxide and then with *N*/10-copper sulphate solution, the non-protein nitrogen being subsequently estimated in the filtrate. Wheat flour contains 2 mg. of amino-acid nitrogen and 6 mg. of amide nitrogen per 100 grams of flour, as well as a considerable amount of non-protein nitrogen in an unknown form. [See also *J. Soc. Chem. Ind.*, 279A.] H. W. B.

Boron. Its Effects on Crops and its Distribution in Plants and Soils in Various Parts of the United States. F. C. COOK and J. B. WILSON (*Proc. Amer. Soc. Biol. Chem.*, 1917, vi—vii; *J. Biol. Chem.*, 1918, **33**).—Boron in the form of borax or colemanite (calcium borate) is an effective larvicide for the housefly; care must be exercised in the subsequent distribution of manure to which it has been added, because small percentages of boron in some soils are found to exert a toxic action on certain plants, especially the *Leguminosae*. [See also *J. Soc. Chem. Ind.*, 274A.] H. W. B.

Organic Chemistry.

Oxidation Products of Paraffin Wax. AKTIEN-GESELLSCHAFT FÜR MINERALÖL-INDUSTRIE VORM. FANTO & Co. (*Zeitsch. angew. Chem.*, 1918, **31**, i, 115).—The method of oxidising paraffin wax by means of atmospheric oxygen was not discovered by Bergmann as he suggests (this vol., i, 285), but by Freund in 1915.

C. A. M.

Besson's Method for the Preparation of Chloroform from Ethyl Alcohol. K. UKITA (*J. Chem. Ind., Tokyo*, 1918, **21**, 219—216).—A stream of chlorine gas is passed into 100 grams of alcohol until the product has D 1·299, when it is added to a mixture of 500 grams of bleaching powder, 100 grams of milk of lime, and 2 litres of water, and the liquid is distilled. The yield is 95—98 grams of chloroform. During the treatment of the alcohol with chlorine, the liquid separates into two layers; the heavy layer increases gradually, and when the chlorination is satisfactory the liquid again becomes homogeneous. J. F. B.

Some Fluoro-bromo-compounds of the Methane and Ethane Series. HANS RATHSBURG (*Ber.*, 1918, **51**, 669—672).—Completely brominated compounds react with silver fluoride to form fluoro-bromo-derivatives. Thus, carbon tetrabromide and silver fluoride in the molecular proportion 1:2 react at above 50—60° to form *fluorotribromomethane*, CBr_3F, as a colourless, heavy, pleasant-smelling liquid, b. p. 107°/760 mm., which is insoluble in water. This reacts with more silver fluoride, best at 140—150°, giving *difluorodibromomethane*, a mobile, readily soluble liquid, b. p. 24·5°/760 mm., m. p. below −80°. Ethyl tribromoacetate and silver fluoride (1:4) react at 190—200° to give *ethyl fluorodibromoacetate*, an insoluble liquid, b. p. 171—173°/760 mm., which is very readily hydrolysed. J. C. W.

Inhibitory Effects of Water on the Interaction of Aluminium and (*a*) the Fatty Acids; (*b*) Phenol, Cresol, and α- and β-Naphthols; (*c*) Methyl, Ethyl, Butyl, Amyl, and Benzyl Alcohols. RICHARD SELIGMAN and PERCY WILLIAMS (*J. Soc. Chem. Ind.*, 1918, **37**, 159—164. Compare A., 1916, ii, 187).—A continuation of work previously recorded. It is definitely shown that when dry fatty acids, dry alcohols, and substances of a phenolic character are heated with aluminium at the boiling point of the substance in question, there is a rapid action between the metal and the organic compound. If, however, a small amount of water is added to the organic compound, the reaction is prevented, or, if it has already commenced, it is at once inhibited. The reaction

has been studied in the case of (i) a mixture of stearic, palmitic, and oleic acids, (ii) phenol, (iii) cresol (commercial), (iv) α-naphthol, (v) β-naphthol, (vi) methyl alcohol, (vii) ethyl alcohol, (viii) butyl alcohol, (ix) amyl alcohol, and (x) benzyl alcohol. The inhibitory action is explained in the following way. The metal is normally protected by the film which covers it, but this film breaks down when exposed to the attack of the dehydrated substances considered. The presence of even the minutest traces of water is sufficient to inhibit the attack, owing either to the fact that the salts, phenoxides, or alkyloxides, as the case may be, are immediately decomposed by water, aluminium hydroxide being formed, or because the aluminium exposed by the breakdown of the film is immediately reoxidised by water (compare also Gladstone and Tribe, T., 1881, **39**, 9; 1882, **41**, 155). J. F. S.

The Decomposition of Glycerol in the Presence of Different Catalysts: Formation of Ethyl and Allyl Alcohols. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1918, **166**, 1033—1039).—The three catalysts used were alumina as a dehydrating catalyst, finely divided copper as a dehydrogenating catalyst, and uranous oxide as a mixed catalyst, capable of producing the two effects. When the vapours of glycerol are passed over alumina at 360°, the products are carbon monoxide, methane, and a trace of carbon dioxide, together with acraldehyde, which undergoes crotonisation, giving higher aldehydes. Passed over finely divided copper at 330°, the glycerol vapour is decomposed, giving as gaseous products hydrogen and carbon dioxide mixed with some methane and carbon monoxide. The liquid products are ethyl alcohol, allyl alcohol, and some of the higher alcohols. With uranous oxide, more ethyl alcohol and less allyl alcohol are obtained, and more acraldehyde. Further, the proportion of carbon dioxide in the gaseous products is increased. By hydrogenation with nickel at 300°, the products are water and the following gases: hydrogen, methane, ethane, and carbon monoxide and dioxide. W. G.

The Action of Fumaryl Chloride on Fumaric Acid. G. C. A. VAN DORP and P. J. MONTAGNE (*Rec. trav. chim.*, 1918, **37**, 294—301. Compare *ibid.*, 1906, **25**, 96).—When fumaryl chloride and fumaric acid are heated together at 165° and the products of the reaction separated by means of benzene and treated with aniline, there are obtained maleinanilic acid, fumarodianilide, fumaranilic acid, and fumaric acid. The authors suggest that the condensation of fumaryl chloride and fumaric acid first gives rise to a compound,

$$COCl\cdot CH_2\cdot CO\cdot O\cdot CO\cdot CH_2\cdot CO_2H,$$

which with another molecule of fumaryl chloride gives the compound $COCl\cdot CH_2\cdot CO\cdot O\cdot CO\cdot CH_2\cdot CO\cdot O\cdot CO\cdot CH_2\cdot COCl$, and this may be decomposed by aniline to give fumarodianilide and fumaranilic acid, whilst the intermediate compound gives either fumarodianilide and fumaric acid or fumaranilic acid. W. G.

Methyltetronic Acid and its Amide. C. S. HUDSON and L. H. CHERNOFF (*J. Amer. Chem. Soc.*, 1918, **40**, 1005—1007).—Methyltetronolactone was readily prepared by bubbling air through an aqueous solution of rhamnose containing potassium hydroxide. So prepared, it has m. p. 123°, $[\alpha]_D -44 \cdot 7°$. When dry ammonia was passed through an ethereal solution of the lactone, *methyltetronamide*, m. p. 135° (decomp.), $[\alpha]_D +54 \cdot 8°$, was obtained.

[EDGAR T. WHERRY.]—Methyltetronolactone has n_a 1·500; n_β 1·515; n_γ 1·535; double refraction strong, 0·035. The axial angle is large, 2E = 120° ± 10°. Sign, positive. Methyltetronamide has n_a 1·510; n_β 1·530; n_γ 1·560; double refraction very strong, 0·050. W. G.

The Isomeric Tetra-acetates of *l*-Arabinose and β-Triacetylmethyl *l*-Arabinoside. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1918, **40**, 992—997. Compare Chavanne, A., 1902, i, 346).—By the acetylation of *l*-arabinose with acetic anhydride and sodium acetate, *α-l-arabinose tetra-acetate*, m. p. 97° (corr.), $[\alpha]_D^{20} +42 \cdot 5°$, was obtained. This tetra-acetate when heated on a water-bath with acetic anhydride and zinc chloride gave the isomeric *β-l-arabinose tetra-acetate*, m. p. 86°, $[\alpha]_D^{20} +147 \cdot 2°$. (corr.), Attempts to prepare α-triacetylmethyl *l*-arabinoside in a crystalline form from either bromoacetyl *l*-arabinose or α-methyl *l*-arabinoside were not successful, but *β-triacetylmethyl l-arabinoside*, m. p. 85° (corr.), $[\alpha]_D^{20} +182 \cdot 0°$, was readily obtained by acetylating β-methyl *l*-arabinoside. W. G.

Triacetyl-*d*-xylose and *d*-Triacetylmethyl *d*-Xyloside. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1918, **40**, 997—1001).—Bromoacetylxylose when shaken with silver carbonate in acetone solution yielded *triacetyl-d-xylose*, m. p. 138—141° (corr.), having initial rotation $[\alpha]_D^{20} +70 \cdot 28°$, which dropped after ten days to 40·8°. This compound, when boiled with acetic anhydride and sodium acetate, yielded β-tetracetyl-*d*-xylose. α-Methyl *d*-xyloside on acetylation yielded *α-triacetylmethyl d-xyloside*, m. p. 86° (corr.), $[\alpha]_D^{20} +119 \cdot 55°$. β-Triacetylmethyl *d*-xyloside was similarly prepared. W. G.

The Glucosazone Reaction. IRA D. GARARD and H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 955—969).—A study of the conditions governing the yield of glucosazone in the osazone test. The authors find that the correct m. p. of phenylglucosazone is 208·0° (corr.), regardless of the method of purification. The maximum yield is obtained when the concentration of phenylhydrazine is about 2·0 grams in 20 c.c. The efficiency of the reagent depends on the acidity, and is independent of the negative ion used. The maximum lies close to $P_{H^+} = 4 \cdot 7$, and is best secured with acetic acid and sodium acetate. Within fairly wide limits, the weight of sugar used has very little effect on the per-

centage yield of osazone. Maltose and dextrin retard the formation of glucosazone, and lactose retards it to a still greater extent, whilst starch has very little effect on its formation. The reaction is not complete in less than three hours. W. G.

The Oxidation of Maltose in Alkaline Solution by Hydrogen Peroxide and by Air. The Preparation and Study of Maltobionic Acid. J. W. E. GLATTFELD and MILTON T. HANKE (*J. Amer. Chem. Soc.*, 1918, **40**, 973—992. Compare Lewis and Buckborough, A., 1914, i, 1199).—The following products of the oxidation of maltose hydrate by hydrogen peroxide in the presence of potassium hydroxide were isolated or detected: formic acid, dextrose, *d*-erythronolactone, *d*-arabonic acid, glycollic, oxalic, and saccharinic acids. By oxidation with a rapid current of air in the presence of the alkali, glyceric acid was also produced.

Maltobionic acid was prepared by the oxidation of maltose by bromine in aqueous solution in the presence of lead carbonate at the ordinary temperature. The acid was isolated as its calcium salt, which had $[\alpha]_D^{20}$ +97·5°. The free acid in aqueous solution had $[\alpha]_D^{20}$ +98·3°. When hydrolysed with $N/5$-sulphuric acid, it gave gluconic acid and dextrose. It formed a *brucine* salt, m. p. 153°, $[\alpha]_D^{20}$ +38·05°. W. G.

Direct Transformation of Secondary and Tertiary Amines into Nitriles. ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 996—997).—The method used to transform di- and tri-*iso*amylamine into *iso*valeronitrile by passing their vapours over finely divided nickel at 350—380° (compare A., 1917, i, 686) is shown to be generally applicable to secondary and tertiary aliphatic amines. Successful results were obtained with di- and tri-hexylamine, di- and tri-amylamine, di- and tri-butylamine, and di- and tri-propylamine. W. G.

Phosphotungstates of certain Bases and Amino-acids. JACK CECIL DRUMMOND (*Biochem. J.*, 1918, **12**, 5—24).—The phosphotungstates of bases and amino-acids yield figures on analysis which agree with the composition indicated by the formula $R_3,H_3PO_4,12WO_3,xH_2O$, where R is a univalent base. They are readily prepared by the addition of a very slight excess of 30% phosphotungstic acid solution to a solution of the base or its salt in 5% sulphuric acid. The best solvents for recrystallisation are water and 50% alcohol. *Lysine phosphotungstate* crystallises in anhydrous needles; crystalline *phosphotungstates* of *trimethylamine* (octahedra), *isobutylamine* (rhombic prisms), *isoamylamine*, *triisobutylamine*, *tripropylamine*, and *triisoamylamine* have also been obtained. *Putrescine* and *cadaverine phosphotungstates* closely resemble those of other bases in crystalline form and solubility. They readily dissolve in acetone, but in water they are all practically insoluble. *Phenylethylamine phosphotungstate* crystallises in yellow prisms, p-*hydroxyphenylethylamine phospho-*

tungstate in anhydrous, orange-red octahedra, *β-iminoazolylethylamine* and *indole-ethylamine phosphotungstates* in colourless prisms and brownish-purple needles respectively. The *phosphotungstate* of *adenine* crystallises in sulphur-yellow cubical or whetstone-shaped plates, of *hypoxanthine* and of *xanthine* in straw-coloured, cubical plates, and of *uric acid* in reddish-brown cubical plates. These purine phosphotungstates are characterised by very slight solubility, even in acetone. The *phosphotungstates* of *betaine*, *stachydrine*, *nicotinic acid*, *choline*, *colamine* (*amino-ethyl alcohol*), *urea*, and *guanidine* all crystallise in the form of rhombic prisms.

The study of the solubilities, crystalline forms, and other properties of these phosphotungstates indicates that they are not likely to be of much help in the identification of the parent bases, because of the lack of individual characteristics. The maximum precipitation usually occurs when a slight excess of phosphotungstic acid is added, and the final liquid contains 5% of sulphuric acid.

H. W. B.

Preparation and Attempts at Cyclisation of Dedimethylpiperidine [Dimethylamino-Δ^{a}-pentene]. AMAND VALEUR and EMILE LUCE (*Bull. Soc. chim.*, 1918, [iv], **23**, 182—185. Compare this vol., i, 102, 158).—Dimethylamino-Δ^{a}-pentene may be prepared by shaking dimethylpiperidinium iodide in aqueous solution with moist silver oxide for three days. After filtering off the silver iodide formed, the alkaline liquid is concentrated under reduced pressure, and finally distilled. Attempts to produce ring formation by heating the base with sulphuric acid, by the action of hypochlorous acid, or by the action of hydriodic acid were not successful.

W. G.

Preparation of some Salts of β-Hydroxytrimethylenediglycine. HUGO KRAUSE (*Ber.*, 1918, **51**, 542—554. Compare this vol., i, 156).—The following additional salts of β-hydroxytrimethylenediglycine, $OH\cdot CH(CH_2\cdot NH\cdot CH_2\cdot CO_2H)_2$, have been prepared: *potassium*, $1H_2O$, and *ammonium* salts, very hygroscopic; a *barium* salt with $1\cdot5H_2O$, by double decomposition of the potassium salt and barium acetate in formalin solution; a comparatively stable *zinc* salt, $C_7H_{12}O_5N_2Zn,EtOH,H_2O$, precipitated by adding alcohol to a mixture of formalin and zinc glycine which had been left for ten hours at 50°; another blue *copper* salt, $1H_2O$, which is extremely soluble, but decomposes in solution at below 50°, mainly according to the equation $C_7H_{12}O_5N_2Cu + 2H_2O = Cu(C_3H_6O_3N)_2 + MeOH$, the metallic *salt* ($0\cdot5H_2O$) being precipitated as a crystalline, blue powder; mixtures of the mercurous and mercuric salts of the acid corresponding with the last copper salt (hydroxymethylglycine?) were obtained by the action of yellow mercuric oxide on β-hydroxytrimethylenediglycine.

Lead gives rise to some characteristic salts. When alcohol is added to a mixture of formalin and a concentrated solution of

lead glycine after leaving for ten hours at 50—55°, or to a mixture of the calcium salt and lead nitrate dissolved in formalin, methyl alcohol is expelled and the crystalline *salt*, $Pb(C_3H_6O_3N)_2$, deposited. This becomes oily on kneading with water, and soon changes into the brilliant white *basic* salt, $2PbX_2,Pb(OH)X,H_2O$ ($X=C_3H_6O_3N$). Solid lead glycine and formalin produce a third *salt*, $Pb(O{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CH_2)_2O$, which crystallises in glistening, microscopic spangles. J. C. W.

Dissociation Constants of some Higher Members of the α-Oximino-fatty Acids. CEDRIC STANTON HICKS (T., 1918, **113**, 554—558).—Measurements have been made of the electrical conductivity of solutions of various α-oximino-fatty acids at dilutions varying from 16 to 256. The conductivity increases with time, but comparable values of the ionisation constants were obtained. The progress of the decomposition was investigated in the case of α-oximino*iso*valeric acid by titration with alkali.

The resnlts obtained are discussed in relation to the constitution of the acids, and it is suggested that the oximinic hydroxyl group acts as a negative substituent and not as an alcoholic group, as was implied by Hantzsch and Miolati. H. M. D.

The Amide Function. J. BOUGAULT (*Compt. rend.*, 1918, **166**, 955—957).—From a comparison of the behaviour and mode of formation of amides with those of acidylsemicarbazinic acids and acidylhydroxamic acids (compare A., 1916, i, 764, 765; 1917, i, 417, 688, 694), the author considers that the constitution of amides is better represented by the formula $R{\cdot}C{<}^{OH}_{NH}$ (acid type) than by the ordinary formula $R{\cdot}CO{\cdot}NH_2$ (basic type). This would explain the existence of metallic derivatives and of Pinner's imino-ethers. W. G.

The Preparation of Fumaronitrile. The Action of Hydroxylamine on Fumaronitrile. L. MCMASTER and F. B. LANGRECK (*J. Amer. Chem. Soc.*, 1918, **40**, 970—973).—The best yield (25%) of fumaronitrile was obtained by heating fumaramide with phosphoric oxide in a current of nitrogen at 170°. With hydroxylamine, the nitrile gave *fumaric acid diamidoxime*, colourless needles, m. p. 212° (decomp.), together with a small amount of a yellow, cotton-like *compound*, m. p. 105° (decomp.), which rapidly darkens in the air. W. G.

The Stability of Cyclic Systems. J. BÖESEKEN [with (MLLE.) M. DE GROOT and W. VAN LOOKEREN CAMPAGNE (*Rec. trav. chim.*, 1918, **37**, 255—265).—The mixture of *cyclo*hexadienes prepared from 1:2-dibromo*cyclo*hexane is, like *cyclo*hexene (compare Böeseken and Sillevis, A., 1914, i, 154), when passed as vapour, mixed with carbon dioxide, over reduced nickel at 180°, converted into benzene and *cyclo*hexane in accordance with the equation $3C_6H_8=C_6H_{12}+2C_6H_6$.

An examination of the behaviour of *cyclo*butane-1 : 1-dicarboxylic acid, *cyclo*butanecarboxylic acid and its amide, and *cyclo*butylamine towards hydrogen in the presence of finely divided platinum shows that all these substances resist hydrogenation, the *cyclo*butane ring being, therefore, quite stable under these conditions.
W. G.

Catalytic Reduction of Organic Halogen Compounds. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1918, **51**, 578—585).—The removal of halogen from organic compounds by the action of hydrogen in the presence of a catalyst has been the subject of a number of papers in recent years, and has actually been developed into methods for estimating halogens (see Borsche and Heimbürger, A., 1915, i, 527, 640; Busch and Stöve, A., 1916, ii, 534; Kelber, A., 1917, ii, 215). The authors have also been engaged on this work, and now make a useful summary of their results.

They find that colloidal palladium protected by gum arabic, or palladinised barium sulphate is an efficient catalyst, and that it is usually advisable to have an alkali present to neutralise the halogen hydracid as it is formed. Many substances react even if merely suspended in aqueous alkalis. In the case of halogen derivatives of ethylenic compounds, the halogen may sometimes be removed without saturating the double linking or the halogen derivative of the saturated compound may be formed. Frequently, the reaction proceeds smoothly to hydrogenation and removal of halogen. In the case of dihalogen compounds, it is apparently impossible to obtain mono-derivatives.

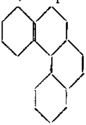
As illustrations, the following reductions are described: bromobenzene to benzene; *o*-bromobenzoic acid to benzoic acid; 1:4-bromonitrobenzene to aniline; chlorocaffeine to caffeine; chlorocrotonic acid to crotonic acid; *o*-chlorocinnamic acid to β-phenylpropionic acid; dibromosuccinic acid to succinic acid. J. C. W.

***p*-Cymene. I. Nitration. Mononitrocymene.** C. E. ANDREWS (*J. Ind. Eng. Chem.*, 1918, **10**, 453—456).—*p*-Cymene was nitrated by mixing it with an equal weight of sulphuric acid, cooling to 0°, and adding a mixture of nitric and sulphuric acids, the temperature being kept at 0°, or lower. The yield of mononitrocymene was 85%; small quantities of *p*-toluic acid and *p*-tolyl methyl ketone were formed during the nitration. The nitrocymene was reduced to the corresponding amine, which (and also the nitro-compound) consisted of the 1:2:4-isomeride. [See, further, *J. Soc. Chem. Ind.*, 1918, August.] W. P. S.

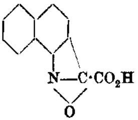
Naphthylacetic Acids. II. 3 : 4-Benzphenanthrene. FRITZ MAYER and TRUDI OPPENHEIMER (*Ber.*, 1918, **51**, 510—516).—Weitzenböck and Lieb briefly outlined the most rational method for the synthesis of 3:4-benzphenanthrene from β-naphthylacetic acid (A., 1912, i, 548), but this parent substance has since become

more readily available (A., 1916, i, 816), and the synthesis has now been examined in detail.

Sodium β-naphthylacetate, *o*-nitrobenzaldehyde, and acetic anhydride are heated for some hours at 120—130°, the *o*-nitro-α-2-naphthylcinnamic acid, m. p. 177—178°, so formed is reduced by ferrous sulphate and ammonia to the *o*-amino-acid, m. p. 191—192°, which is diazotised and shaken with copper powder, when 3:4-benzphenanthrene-1-carboxylic acid, m. p. 218°, is produced. When distilled at 400° in a current of carbon dioxide, this acid gives a poor yield of 3:4-benzphenanthrene (I), crystallising in needles or leaflets, m. p. 158—160°, and forming a red *picrate*, m. p. 140—141°.



(I.)



(II.)

Potassium 1-nitro-2-naphthylacetate loses water when heated with acetic anhydride and zinc chloride, and cannot, therefore, be made to condense with benzaldehyde. The product is *naphthanthroxanic acid* (II), m. p. 218°.

In the above synthesis, there is a possibility of the condensation of the *o*-amino-α-2-naphthylcinnamic acid leading alternatively to a naphthanthracenecarboxylic acid. Small quantities of by-products are, indeed, formed, but it is difficult to isolate sufficient to ascribe any definite constitution to them. J. C. W.

Some Halogen Derivatives of Aromatic Amines and their Analysis. I. F. B. DAINS, T. H. VAUGHAN, and W. M. JANNEY (*J. Amer. Chem. Soc.*, 1918, **40**, 930—936. Compare Wheeler, A., 1910, i, 17, 19, 662; 1911, i, 27).—Iodine reacts with chloro- and bromo-anilines to give iodo-derivatives. Thus *p*-bromoaniline gives 4-*bromo-2-iodoaniline*, m. p. 71°, yielding a *hydrochloride*, m. p. 205—206°; an *acetyl* derivative, m. p. 148°; a *benzoyl* derivative, m. p. 152°; 4-*bromo-2-iododiphenylthiocarbamide*, m. p. 167°; 4-*bromo-2-iodophenylallylthiocarbamide*, m. p. 177°; 4-*bromo-2-iodophenylcarbamide*, m. p. 167°; *anisylidene-4-bromo-2-iodoaniline*, m. p. 118°; *cinnamylidene-4-bromo-2-iodoaniline*, m. p. 96°; *piperonylidene-4-bromo-2-iodoaniline*, m. p. 120°; and o-*nitrobenzylidene-4-bromo-2-iodoaniline*, m. p. 159°. If in the above preparation 2 mols. of iodine are used, the product is a mixture of 4-bromo-2-iodoaniline and 4-*bromo-2:6-di-iodoaniline*, m. p. 148°.

From *m*-bromoaniline, a 3-*bromoiodoaniline*, m. p. 56°, giving a *hydrochloride*, m. p. 192°, and an *acetyl* derivative, m. p. 199°, is obtained in which the position of the entrant iodine atom has not been definitely ascertained.

p-Chloroaniline yields *4-chloro-2(?)-iodoaniline*, m. p. 46°, giving a *hydrochloride*, m. p. 202°, an *acetyl* derivative, m. p. 150°, and a *benzoyl* derivative, m. p. 145°. *4-Chlorodi-iodoaniline*, m. p. 129°, giving a *benzoyl* derivative, m. p. 205°, was also prepared.

o-Chloroaniline yielded 2-chloro-4-iodoaniline (compare Werner and Caldwell, T., 1907, **91**, 246). It gave a *hydrochloride*, m. p. 190°, a *benzanilide*, m. p. 165°, and a *phenylcarbamide*, m. p. 175°.

m-Chloroaniline yielded with iodine *3-chloro-4-iodoaniline*, m. p. 65°, giving a *hydrochloride*, m. p. 180°, an *acetyl* derivative, m. p. 170°, and a *benzoyl* derivative, m. p. 144°. The base when diazotised and treated with potassium iodide gave *2-chloro-1:4-di-iodobenzene*, m. p. 51°, similar to that obtained in the same way from 2-chloro-4-iodoaniline.

2:4-Dichloroaniline only undergoes iodination with difficulty, yielding a small amount of *2:4-dichloro-6(?)-iodoaniline*, m. p. 85°, giving a *hydrochloride*, m. p. 180°.

In the majority of the above cases the yields were good, but if the hydrogen of the ring is replaced by two or three methyl groups or by a methoxy-, ethoxy-, or acetylamino-group, the yield of the iodo-derivative was poor, or only resinous products were obtained. The same is true of the methyl- and dimethyl-anilines. Thus ψ-cumidine only gave a small yield of 2-iodo-3:4:6-trimethylaniline, m. p. 93°. *o*-Anisidine gave *4(?)-iodo-2-methoxyaniline*, m. p. 49°, giving a *hydrochloride*, m. p. 180°, and an *acetyl* derivative, m. p. 176°. *p*-Anisidine only gave a black, waxy, resinous substance, and acetyl-*p*-phenylenediamine behaved in a similar manner.

For the estimation of the halogens in these and similar halogen derivatives, the authors advocate a slight modification of Chablay's method (compare A., 1907, ii, 195), the compound being decomposed by sodium in liquid ammonia. [For details, see *J. Soc. Chem. Ind.*, August.] W. G.

Phenylcarbamates of Terpenic Alcohols and Phenols. F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 266—269).—Phenylcarbamates may be readily obtained in a crystalline state by boiling the alcohol or phenol with the requisite amount of phenylcarbimide in light petroleum (b. p. 170—200°) for a half to one hour. In this way, excellent results were obtained with the three cresols, thymol, menthol, borneol, and eugenol, but good results were not obtained with geraniol or linalool. Camphor may be separated from borneol by this method, the unattacked camphor remaining in solution in the solvent on cooling, whilst the bornyl phenylcarbamate crystallises out. W. G.

Peculiar Action of Methyl Alcohol containing Sulphuric Acid on a β-Arylhydroxylamine. EUG. BAMBERGER (*Ber.*, 1918, **51**, 629—634).—When *m*-2-xylylhydroxylamine is left with a mixture of methyl alcohol and a little concentrated sulphuric acid,

the main product is 5-methoxy-*m*-2-xylidine (A., 1903, i, 624), but this is accompanied by a small quantity of a neutral substance, ammonia being formed as well. The isolation of this compound in a yield of about 4·5% is now described. It is referred to as an "*oxide*," and it crystallises from acetone in glassy prisms, m. p. 139—140°, contains a methoxyl group but no hydroxyl group, and changes into formaldehyde and *m*-2-xylenol when heated at 250—260°. Its formation and constitution are provisionally represented thus:

$$C_6H_3Me_2\cdot NH\cdot OH + MeOH = OMe\cdot C\begin{cases} CMe\colon CH \\ \quad O \\ CMe\colon CH \end{cases}CH + NH_3.$$

J. C. W.

Acetylation of β-Phenylhydroxylamine. EUG. BAMBERGER (*Ber.*, 1918, **51**, 636—640).—Phenylhydroxylamine can be readily converted into its N-acetyl derivative by means of acetic anhydride, and the reaction can be adapted to the detection of the base, as follows. A few mg. of the substance are dissolved in cold water; three separate drops of acetic anhydride are added at half-minute intervals, with shaking, followed by a drop of very dilute ferric chloride, when the violet-red colour, changing into grey and then bluish-green, characteristic of the acetyl derivative, develops (see A., 1902, i, 539).

For quantitative purposes, thioacetic acid is a better acetylating agent. The reagents are mixed in dry alcohol, left for a few days, when the solvent is evaporated, the residue rendered alkaline and shaken with ether to remove by-products, and then the solution is acidified and extracted with ether. N-Acetylphenylhydroxylamine (*ibid.*) is soluble in ammonia solution and in 2*N*-sodium carbonate.

Diacetylphenylhydroxylamine, $C_6H_5\cdot NAc\cdot OAc$, glassy prisms, m. p. 43°, is the product when the base is left with an excess of acetic anhydride. J. C. W.

The Electrolytic Reduction of *p*-Aminophenol. T. SHŌJI (*J. Chem. Ind., Tokyo*, 1918, **21**, 117—136).—The principal product of the electrolytic reduction of nitrobenzene in presence of strong sulphuric acid with platinum electrodes is *p*-aminophenol; the use of a carbon cathode is permissible. The concentration of the sulphuric acid electrolyte must not exceed 80%, otherwise there will be a loss of aminophenol by sulphonation. The quantity of sulphuric acid should be five times that of the nitrobenzene; the temperature must be kept at about 80°; a higher temperature induces sulphonation. The current density is 8—9 amperes per sq. dcm., and the *E.M.F.* 6—8 volts. Vigorous agitation of the electrolyte is most important for obtaining a good current efficiency. The cathode chamber must be kept closed to prevent loss of nitrobenzene by volatilisation. Under these conditions, the author obtained 80 grams of crude *p*-aminophenol sulphate from 100

grams of commercial nitrobenzene, yielding 38 grams of free base, or 43% of the theoretical quantity. J. F. B.

β-Cholestanol, some of its Derivatives and Oxidation Products. GEORGE WILLIAM ELLIS and JOHN ADDYMAN GARDNER (*Biochem. J.*, 1918, **12**, 72—80).—The following derivatives of β-cholestanol have been prepared: *chloroacetate*, $C_{29}H_{49}O_2Cl$, by the action of chloroacetyl chloride in chloroform solution, glistening plates from a mixture of chloroform and ethyl acetate, m. p. 178—179°; *benzoate*, $C_{34}H_{52}O_2$, by the action of benzoyl chloride in pyridine solution, crystallising from ethyl acetate in small plates. It melts at 155° with brilliant fluorescence during the rise of temperature from about 138° to 155°, $[\alpha]_D^{23}$ +23·3° in chloroform solution; *stearate*, $C_{45}H_{82}O_2$, by boiling with stearyl chloride in chloroform solution, flaky crystals from a mixture of alcohol and chloroform, m. p. 100°, $[\alpha]_D^{20}$ +18·4° in ether solution.

On oxidation, β-cholestanol yields β-cholestanone (Diels and Abderhalden, A., 1906, i, 272), which on further oxidation with ammonium persulphate has been found to give a number of lactones of the formula $C_{27}H_{46}O_2$, of which three have been isolated in a more or less pure state and found to melt at 98—100°, 159—161°, and 201—202° respectively. These substances are different, however, from those prepared in a similar manner from coprostanone (Gardner and Goddard, A., 1914, i, 169). H. W. B.

Preparation of Benzoic Acid. WESTON CHEMICAL CO., and J. SAVAGE (Brit. Pat. 116348).—Toluene is converted into benzyl chloride, with traces of benzylidene chloride, by chlorination at the boiling point; the benzyl chloride is converted into benzyl alcohol by boiling with sodium hydroxide solution or milk of lime, and the alcohol is oxidised to alkali benzoate by means of a hypochlorite in presence of alkali. A. S.

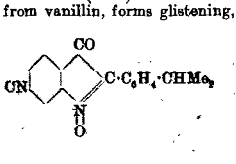
Catalytic Action of Colloidal Metals of the Platinum Group. XVI. Partial Reduction of Phenylpropiolic Acid with Colloidal Platinum. C. PAAL and ANTON SCHWARZ (*Ber.*, 1918, **51**, 640—643).—It has already been shown that the hydrogenation of phenylpropiolic acid and acetylene can be so controlled under certain conditions, using colloidal palladium as the catalyst, that the corresponding ethylenic compounds are the main products (A., 1909, i, 926; 1915, i, 113). In the case of acetylene, it has also been shown that colloidal platinum is less efficient, and that a mixture of ethylene, ethane, and unreduced acetylene is generally obtained (A., 1915, i, 765). The hydrogenation of phenylpropiolic acid by means of colloidal platinum has now been studied. The yield of maleinoid forms of cinnamic acid is found to be much less than when palladium is used, but no β-phenylpropionic acid could be detected under the conditions employed. The deficiency is largely due to the formation of indefinite by-products. J. C. W.

The Border-line between Isomerism and Polymorphism. III. PAUL PFEIFFER [with J. KLINKERT] (*Ber.*, 1918, **51**, 554—567. Compare A., 1916, i, 24; 1917, i, 140).—It has been shown that certain nitromethoxystilbenes exhibit a kind of isomerism which is termed "cryptoisomerism," and this communication records some further experiments designed to find what conditions are necessary for the display of this phenomenon. It is shown, on the one hand, that the nitro-group may be in the ortho- or para-position in the one benzene nucleus (the question of the meta-position is not discussed), and that, on the other hand, a hydroxyl or methoxyl group, but not alkyl or acyloxyl, must be in the para-, but not the ortho-, position in the other benzene nucleus. That is, besides the chromophores, nitro-group and ethylene linking, there must be an auxochrome.

4-Nitro-3-cyanostilbene, obtained by heating *p*-nitro-*m*-toluonitrile with benzaldehyde and a few drops of piperidine at 140°, crystallises in golden-yellow, flat needles, m. p. 187°, and may be hydrolysed by boiling with aqueous-alcoholic potassium hydroxide to *4-nitrostilbene-3-carboxylic acid*, pale yellow, glistening leaflets, m. p. 203°. *4-Nitro-3-cyano-4'-*iso*propylstilbene*, from cuminaldehyde, forms golden-yellow leaflets, m. p. 132—133°, and *4-nitro-3-cyano-4'-methoxystilbene*, from anisaldehyde, crystallises in brownish-orange, glistening leaflets, m. p. 161°.

p-Nitro-*o*-toluonitrile gives rise to *4-nitro-2-cyano-4'-*iso*propylstilbene*, orange-yellow needles, m. p. 195°, and 4-nitro-2-cyano-4'-hydroxystilbene (*ibid.*, 140). The latter crystallises from glacial acetic acid in orange-yellow needles, m. p. 226°, but if the solution is poured into water, a pure yellow variety is deposited, which becomes permanently orange-yellow on heating at about 200°. It also forms an acetate (*ibid.*) and a *benzoate*, glistening, yellow, flat needles, m. p. 178°.

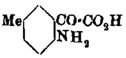
o-Nitro-*p*-toluonitrile is the parent of the following derivatives: *2-Nitro-4-cyano-4'-*iso*propylstilbene*, which crystallises with 0·5 mol. AcOH in flat, yellow needles, m. p. 134—138° (142° when deprived of crystal solvent). *2-Nitro-4-cyano-4'-hydroxystilbene*, which exists in two forms, an orange-yellow, giving a pale orange-yellow hydrate, and an orange-red, giving an orange solvate with 1AcOH; the two forms exhibit the same colour in any particular solvent, but the shades vary with the solvent; they both have the same colour at 210° and melt at 230—231°; the acetate has m. p. 225°, not 186° (*ibid.*). *2-Nitro-4-cyano-4'-hydroxy-3'-methoxystilbene*, from vanillin, forms glistening, orange needles, m. p. 207°, and its *acetate*, yellow leaflets, m. p. 170°.

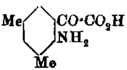


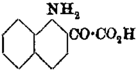
The above 2-nitro-4-cyano-4'-*iso*propylstilbene yields a mixture of chlorides (m. p. 120—125° and 150°) when treated with chlorine in carbon disulphide. When a solution of these in pyridine is exposed to sunlight, *6-cyano-4'-*iso*propyl-2-*

phenylisatogen (annexed formula) is deposited, in orange-red needles, m. p. 220° (compare A., 1916, i, 327). J. C. W.

The Isatoic Acids. J. MARTINET (*Compt. rend.*, 1918, **166**, 952—955).—Three isatoic acids have been obtained by dissolving the corresponding isatins in a known volume of standard potassium hydroxide, and, after the liquid has turned yellow, cooling and adding the calculated quantity of hydrochloric acid. The voluminous precipitate is collected and dried rapidly over phosphoric oxide. In this way, 5-methylisatin yielded 5-*methylisatoic acid* (6-*amino*-m-*tolylglyoxylic acid*) (formula I), m. p. 132°; 5:7-dimethylisatin gave 5:7-*dimethylisatoic acid* [2-*amino*-3:5-*dimethylphenylglyoxylic acid*] (formula II), an orange-yellow, crystalline powder, m. p. 215°; α-naphthisatin gave α-*naphthisatoic acid* [α-*aminonaphthyl*-β-*glyoxylic acid*] (formula III), m. p. 187°.


(I.)


(II.)


(III.)

These acids give citron-yellow *potassium* and *barium* salts, orange-yellow *lead* salts, red *copper* salts, and pale yellow *silver* salts. W. G.

Tetraiodophenolphthalein and Tetrachlorotetraiodophenolphthalein and some of their Derivatives. W. R. ORNDORFF and S. A. MAHOOD (*J. Amer. Chem. Soc.*, 1918, **40**, 937—955).—Tetraiodophenolphthalein was prepared by the method of Classen and Löb (compare A., 1895, i, 539) with slight modifications, and was finally obtained in the form of colourless needles decomposing at 270—272°. Contrary to the opinion of these two authors, the corresponding free carbinolcarboxylic acid could not be obtained, although its potassium and disodium salts were prepared. These salts when heated gave the corresponding salts of tetraiodophenolphthalein. When dry ammonia was passed over the phthalein, a *tetra-ammonia* salt, $C_{20}H_{10}O_4I_4,4NH_3$, was obtained. Tetraiodophenolphthalein gave a *diacetate*, m. p. 246°, a *dibenzoate*, m. p. 298°, and an *oxime*, m. p. 170°.

By the iodination of tetrachlorophenolphthalein in alkaline solution, *tetrachlorotetraiodophenolphthalein*, $\begin{matrix}C_6Cl_4\\CO{\cdot}O\end{matrix}\!>\!C(C_6H_2I_2{\cdot}OH)_2$, decomposing at 240—244°, was obtained, which gave a *diacetate*, m. p. 262°, a *dibenzoate*, m. p. 205°, and with dry ammonia a *tetra-ammonia* salt.

A study of the visible and ultra-violet absorption spectra of these and other phenolphthalein derivatives showed that neutral alcoholic solutions of these phthaleins have absorption spectra of the same type, but that the type changes when the solution becomes alkaline, the characteristic spectrum of the alkaline solutions having

three absorption bands, one at $\lambda = 1600$—1800, the second at $\lambda = 2500$—2700, and the third at $\lambda = 3200$—3600. The magnitude of the first two bands varies greatly with the phthalein. Bromine and iodine in the phenol residues shift all bands towards lower frequencies. Chlorine in the phthalic residue shifts the visible band in the same direction, but the two ultra-violet bands in the opposite direction. The shift increases with the mass of the substituent. W. G.

Anthranil. XXI. Photochemical Formation of *o*-Nitrosobenzaldehyde. EUG. BAMBERGER (*Ber.*, 1918, **51**, 606—612).—Sachs and Hilpert (A., 1904, i, 876) exposed a benzene solution of *o*-nitrobenzyl alcohol to the light, in the hope of obtaining *o*-nitrosobenzaldehyde, according to the scheme:

$$C_6H_4{<}^{NO_2}_{CH_2\cdot OH} \longrightarrow C_6H_4{<}^{NO}_{CH(OH)_2} \longrightarrow C_6H_4{<}^{NO}_{CHO} + H_2O.$$

During 1909 and 1910, the author exposed an ethereal solution to the sunlight for about 830 hours at Davos Platz, and now describes the examination of the product. He finds that *o*-nitrosobenzaldehyde is formed, but that it largely suffers oxidation, on the one hand, to *o*-nitrobenzaldehyde and *o*-nitrobenzoic acid, and reduction, on the other hand, to *o*-nitrosobenzyl alcohol, whence anthranil is formed, and probably *oo'*-azoxybenzaldehyde, whence indazolylbenzoic acid and its lactone. J. C. W.

Anthranil. XXII. *N*-Acetyl-*o*-hydroxylaminobenzaldehyde. EUG. BAMBERGER (*Ber.*, 1918, **51**, 613—629).—The discovery that anthranil is the anhydride of *o*-hydroxylaminobenzaldehyde has naturally led the author to attempt to isolate this compound, but so far it has only been obtained in the form of a very impure, dilute solution (A., 1904, i, 94). The production of the *N*-acetyl derivative is now described, and with this the research is broken off.

"Agnotobenzaldehyde," the primary reduction product of *o*-nitrobenzaldehyde (A., 1907, i, 163), is treated with acetic anhydride, added drop by drop, at 0°, and thus converted into *o*-nitrobenzaldehyde and *N-acetyl-o-hydroxylaminobenzaldehyde*, $CHO\cdot C_6H_4\cdot NAc\cdot OH$, which crystallises from slowly cooling benzene in glassy, triclinic prisms melting at 132° if plunged in a bath at 110° and then heated further, but changing slowly at about 125° into acetylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NHAc$, thus becoming solid again. The compound dissolves in concentrated sulphuric acid with lemon-yellow colour, anthranil being deposited on dilution. An aqueous suspension gives a deep violet-red colour with ferric chloride. It is soluble in alkali hydroxides or carbonates or aqueous ammonia with lemon- to orange-yellow colour, but the solutions suffer obscure changes when kept. The *phenylhydrazone* forms golden-yellow, silky needles, m. p. 120—120·5° (180—181° on one occasion), and dissolves in sodium hydroxide with magenta

colour. When a solution of bleaching powder is slowly added to a cold, supersaturated solution of the aldehyde in water, *o*-nitrosobenzaldehyde is precipitated, the yield being as high as 85%. *o*-Nitrobenzaldehyde is also formed if too much hypochlorite is used, whilst the addition of perhydrol to a solution in glacial acetic acid causes the precipitation of a "*peroxide*" (?),

$$CHO\cdot C_6H_4\cdot NAc\cdot O\cdot OH,$$

in satiny, flat needles, m. p. 110·5—111°, which gives the peroxide reaction with titanium dioxide in sulphuric acid. J. C. W.

Bornylenecamphor and a New Dicamphor, *iso*Dicamphor. MARCEL GUERBET (*Compt. rend.*, 1918, **166**, 1049—1052).—When camphor is heated with sodium methoxide in methyl-alcoholic solution, the main product is not bornylenecamphor, only a trace of this compound being obtained, but *isodicamphor*,

$$C_8H_{14}<\begin{matrix}CH-CH\\ | \quad\quad | \\ CO \quad CO\end{matrix}>C_8H_{14},$$

m. p. 196°, $[\alpha]_D^{15}$ +64°54′ (in alcohol).

At 250° it is slowly converted into camphor. It yields a *monoxime*, m. p. 159—160°, and a *dioxime*, m. p. 235°. On bromination, it gives *bromoisodicamphor*, $C_{20}H_{29}O_2Br$, m. p. 161°, and *dibromoisodicamphor*, m. p. 132°. When oxidised by dilute nitric acid, it yields camphoric acid. W. G.

Nomenclature of Hydrocyanic Glucosides of the Amygdalin Group. EM. BOURQUELOT (*J. Pharm. Chim.*, 1918, [vii], **17**, 359—361).—When hydrolysed with hot concentrated hydrochloric acid, prunasin yields *l*-phenylglycollic acid, prulaurasin gives inactive phenylglycollic acid, and sambunigrin (A., 1905, i, 912) *d*-phenylglycollic acid. Under the same conditions, amygdalin gives the *l*-acid, *iso*amygdalin the inactive acid, and *d*-amygdalin the *d*-acid. The relations of these glucosides is therefore as follows:

Monoglucosides, $C_{14}H_{17}O_6N$	Diglucosides, $C_{20}H_{27}O_{11}N$.
Prunasin	*l*-Amygdalin or gluco-prunasin
Prulaurasin	*iso*Amygdalin or gluco-prulaurasin.
Sambunigrin	*d*-Amygdalin or gluco-sambunigrin.

The diglucosides may be converted into the corresponding monoglucosides by the action of dry bottom-fermentation yeast.

W. P. S.

A New Group of *cyclo*Propane Derivatives. I. Action of Phenylacyl Haloids on 3-Acylcoumarins in the Presence of Sodium Alkyloxides. OSKAR WIDMAN (*Ber.*, 1918, **51**, 533—541). —When 3-acetylcoumarin and ω-halogenoacetophenones are mixed in cold alcohol and treated with one atomic proportion of sodium ethoxide solution, two products are obtained which are indifferent towards permanganate, the ethylene linking in the coumarin ring being saturated by the addition of the phenacylidene residue,

*cyclo*propane derivatives resulting. The chief product is *3-acetyl-3:4-phenacylidenecoumarin*, $\begin{matrix}C_6H_4-CH \\ | \quad\quad | \\ O\cdot CO\cdot CAc\end{matrix}\!\!>CHBz$, which crystallises in silky needles, m. p. 184°, and the other compound, which is the more soluble in alcohol, is *ethyl α-acetyl-αβ-phenacylidene-coumarate* [*ethyl* 1-*acetyl*-2-*benzoyl*-3-o-*hydroxyphenyl*cyclo*pro-pane*-1-*carboxylate*], $CHBz\!<\!\begin{matrix}CAc\cdot CO_2Et \\ CH\cdot C_6H_4\cdot OH\end{matrix}$. This crystallises in brilliant, quadratic prisms, m. p. 117°, and forms an *acetate*, lustrous octahedra, m. p. 89°. The condensation must proceed most readily, for the ω-halogenoacetophenones give rise to the 2-halogeno-3:4-oxido-3:5-diphenyltetrahydrofurans when left with sodium alkyloxides alone (A., 1913, i, 1219), and no trace of these compounds is found in the present instance.

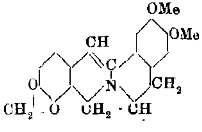
Similar compounds are produced by other 3-acylcoumarins. Thus *3-propionylcoumarin*, very long, silky needles, m. p. 134° (from salicylaldehyde and ethyl propionylacetate) gives rise to *3-propionyl-3:4-phenacylidenecoumarin*, needles, m. p. 157—158°, and *ethyl α-propionyl-αβ-phenacylidenecoumarate*, prisms or irregular hexagonal tablets, m. p. 109—110°. 3-Benzoylcoumarin, m. p. 135—136° (compare Knoevenagel and Arnot, A., 1905, i, 65), forms *3-benzoyl-3:4-phenacylidenecoumarin*, tablets, m. p. 189—190°, there being also a suggestion of *cis-trans*-isomerism in this case. Ethyl coumarin-3-carboxylate forms *ethyl 3:4-phenacyl-idenecoumarin-3-carboxylate*, flat needles, m. p. 176—177°; *methyl coumarin-3-carboxylate*, m. p. 116—117° (from methyl malonate and salicylaldehyde), yields the corresponding *methyl* ester, m. p. 183°, mixed with "*methyl ethyl αβ-phenacylidenesalicylidene-malonate*" [*methyl ethyl* 2-*benzoyl*-3-o-*hydroxyphenyl*cyclo*propane*-1:1-*dicarboxylate*], $\begin{matrix}CO_2Me \\ CO_2Et\end{matrix}\!\!>C<\!\begin{matrix}CHBz \\ CH\cdot C_6H_4\cdot OH\end{matrix}, H_2O$, this being the more soluble in alcohol, and crystallising in glistening rhombo-hedra, m. p. 96°. The 3:4-phenacylidenecoumarin-3-carboxylates are hydrolysed by 4% sodium hydroxide to salicylaldehyde, phen-acylmalonic acid, $CH_2Bz\cdot CH(CO_2H)_2$, and *α-hydroxy-γ-benzoyl-α-o-hydroxyphenylpropane-ββ-dicarboxylic acid*,

$$OH\cdot C_6H_4\cdot CH(OH)\cdot C(CO_2H)_2\cdot CH_2Bz,$$

short prisms, m. p. 126—128° (decomp.). 3-Cyanocoumarin also condenses with ω-bromoacetophenone, yielding *3-cyano-3:4-phen-acylidenecoumarin*, in slender needles, m. p. 218°. J. C. W.

*epi***Berberine.** William Henry Perkin, jun. (T., 1918, **113**, 492—522).—An attempt to prepare *epi*berberinium hydroxide and to compare its properties and those of its salts with those of berberinium hydroxide and its salts (compare T., 1916, **109**, 833). Attempts to demethylate cryptopine by the method of Diels and Fischer as applied to codeine (compare A., 1914, i, 989) were not successful. It was noticed, however, that many methochlorides, such as 6:7-dimethoxy-2-methyltetrahydro*iso*quinoline, decompose

at their melting points, giving off methyl chloride. β-Tetrahydroanhydroberberine methochloride (Pyman, T., 1913, **103**, 828) in this way loses its methyl chloride. *iso*Cryptopine chloride when heated in small quantities under diminished pressure decomposes at 260°, giving methyl chloride and *dihydroanhydro*epi*berberine* (annexed formula), crystallising in iridescent, golden, monoclinic plates [$a:b:c = 1{\cdot}163:1:0{\cdot}995$; $\beta = 97°15'$], m. p. 172—174°. It gives a *hydrochloride*, $C_{20}H_{19}O_4N,HCl,3H_2O$, a *hydrobromide*, a *methosulphate*, m. p. 260° (decomp.), and a *methiodide*, m. p. 245° (decomp.). The methosulphate when boiled with methyl-alcoholic potassium hydroxide yields anhydrocryptopine (T., 1916, **109**, 975). *Tetrahydroanhydro*epi*berberine*, $C_{20}H_{21}O_4N$, m. p. 170—171°, is obtained either by the action of heat on *iso*dihydrocryptopine α-chloride or β-chloride, or by the reduction of dihydroanhydro*epi*berberine with zinc or tin and hydrochloric acid. It is a strong base, and gives a *hydrochloride*, a *sulphate*, a *nitrate*, and a *methosulphate*, m. p. 255—260° (decomp.), which is decomposed by boiling with methyl-alcoholic potassium hydroxide, giving anhydrodihydrocryptopine.



When dihydroanhydro*epi*berberine or the tetrahydro-derivative is acted on by oxidising agents, such as bromine, iodine, or dilute nitric acid, or preferably by mercuric acetate in acetic acid solution, various, deep orange salts of *epi*berberine are obtained by suitable subsequent treatment. In this way, the author has prepared epi*berberinium chloride*, $C_{20}H_{18}O_4NCl,4H_2O$, which gives a *platinichloride*, the *sulphate*, the *iodide*, and the *picrate*, m. p. 222°.

*epi*Berberinium sulphate is decomposed by aqueous sodium hydroxide in the same manner as is berberinium sulphate, and yields *oxy*epi*berberine*, $C_{20}H_{17}O_5N$, m. p. 240—241°, and dihydroanhydro*epi*berberine. Oxy*epi*berberine gives an *acetate*,

$$C_{20}H_{17}O_5N,C_2H_4O_2,$$

which is dissociated by water or heat. By the action of hydrochloric acid, oxy*epi*berberine is converted into iso*oxy*epi*berberine*, needles. Although it was not found possible to isolate *epi*berberine itself, its O-methyl and O-ethyl derivatives have been obtained in a pure condition by the action of sodium methoxide and ethoxide respectively on *epi*berberinium chloride. O-*Methyl*epi*berberine* separates in golden prisms, m. p. 150—152° (decomp.), and O-*ethyl*epi*berberine*, $C_{20}H_{18}O_4(OEt)N$, in needles, m. p. 135—136° (decomp.). Both these compounds dissolve readily in boiling acetone, and from the solution, on cooling, *anhydro*epi*berberineacetone*, $C_{20}H_{17}O_4N,C_3H_6O$, m. p. 162°, separates. The author discusses fully the nomenclature of berberine and its salts. For experimental details, see the original. W. G.

Metallic Derivatives of Alkaloids. JITENDRA NATH RAKSHIT (T., 1918, **113**, 466—471).—Sodium and potassium derivatives of codeine and narcotine and the sodium derivative of cotarnine were obtained by boiling the alkaloids with the respective metals in benzene. *Sodium codeine*, $C_{18}H_{20}O_3NNa$, is a brownish-yellow powder which, in aqueous solution, does not give any precipitate with Mayer's reagent until the mixture is acidified. *Potassium codeine*, $C_{18}H_{20}O_3NK$, forms reddish-brown crystals. *Sodium narcotine*, $C_{22}H_{22}O_7NNa$, was obtained as a reddish-yellow powder, which is decomposed in aqueous solution by carbon dioxide, narcotine being liberated. *Dipotassium narcotine*, $C_{22}H_{21}O_7NK_2$, is a bright yellow, crystalline powder. *Tetrasodium cotarnine*, $C_{12}H_{11}O_4NNa_4$, is a hygroscopic, bright yellow, crystalline powder. *Calcium morphinate*, $(C_{17}H_{18}O_3N)_2Ca$, was obtained by triturating morphine with calcium hydroxide in the presence of alcohol as a brown, non-deliquescent powder, which is readily decomposed by carbon dioxide. W. G.

The Presence of a Fixed Alkaloid in the Common Broom. AMAND VALEUR (*Compt. rend.*, 1918, **167**, 26—28).—From the mother liquors resulting from the crystallisation of sparteine sulphate as prepared from *Sarothamnus scoparius*, the author has isolated another alkaloid, *sarothamnine*, which readily forms crystalline compounds with various solvents. Thus *sarothamnine-chloroform*, $C_{15}H_{24}N_2,\frac{1}{2}CHCl_3$, has m. p. 127° and $[\alpha]_D$ −38·7°; *sarothamnine-ethyl alcohol*, $C_{15}H_{24}N_2,\frac{1}{2}EtOH$, has m. p. 90°, $[\alpha]_D$ −25·6°. It unites similarly with methyl alcohol and benzene. The alkaloid is unsaturated, since it reduces aqueous potassium permanganate in the cold. W. G.

Pyridine Derivatives from αβ-Dichloroethyl Ether and Ethyl β-Aminocrotonate, and related Amino-compounds. II. ERICH BENARY (*Ber.*, 1918, **51**, 567—577. Compare A., 1911, i, 320).—The action of various agents on the 4-chloromethylpyridine derivatives described in the earlier paper, and the production of similar esters from acetylacetonamine and benzoylacetonamine are dealt with in this paper.

The reaction between αβ-dichloroethyl ether and ethyl β-aminocrotonate, whereby ethyl 2 : 6-dimethyl-4-chloromethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate is formed, is best effected in the presence of dilute aqueous ammonia. The ester reacts with potassium hydrosulphide to form the 4-*thiolmethyl* derivative, which crystallises in slender needles, m. p. 86—87°, and with bromine to give a *dibromo-dibromide*, pale yellow needles, m. p. 109—110°, which may be oxidised by pure nitric acid to the corresponding *ethyl dibromo-2 : 6-dimethyl-4-chloromethylpyridine-3 : 5-dicarboxylate dibromide*, $C_{14}H_{16}O_4NClBr_4$, m. p. 114—115°.

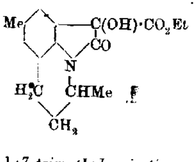
More important results may be obtained with ethyl 2 : 6-dimethyl-4-chloro(or iodo-)methylpyridine-3 : 5-dicarboxylate. Hydrolysis with boiling 10% sodium hydroxide gives rise to the *lactone* of

2 : 6-*dimethyl*-4-*hydroxymethylpyridine*-3 : 5-*dicarboxylic acid*, hard crystals, m. p. 213°. With alcoholic ammonia at 100—110°, the product is the *lactam* of *ethyl hydrogen* 2 : 6-*dimethyl*-4-*amino-methylpyridine*-3 : 5-*dicarboxylate*, needles, m. p. 168—169°, which may be hydrolysed by boiling alcoholic potassium hydroxide to the free *lactamic acid*, $\begin{array}{l}\text{CMe}\cdot\text{C(CO}_2\text{H):C}\cdot\text{CH}_2\\ \text{N}\cdot\text{CMe}=\!=\!=\!=\text{C—CO}\end{array}\!\!>\!\text{NH}$, pale yellow, microscopic needles, decomp. 300°. Potassium hydrosulphide forms the *thiolactone* of *ethyl hydrogen* 2 : 6-*dimethyl*-4-*thiolmethylpyridine*-3 : 5-*dicarboxylate*, in long, silky, pale pink needles, m. p. 115—116°, and this may be hydrolysed to the free *thiolactonic acid*, decomp. 272°. Potassium cyanide produces *ethyl* 2 : 6-*dimethyl*-4-*cyano-methylpyridine*-3 : 5-*dicarboxylate*, in colourless needles, m. p. 66—67°.

Acetylacetonamine and $\alpha\beta$-dichloroethyl ether react in the presence of dilute aqueous ammonia to form 3 : 5-*diacetyl*-2 : 6-*dimethyl*-4-*chloromethyl*-1 : 4-*dihydropyridine*, pale yellow, hard needles, m. p. 151°, which may be oxidised by nitric acid to 3 : 5-*diacetyl*-2 : 6-*dimethyl*-4-*chloromethylpyridine*, colourless needles, m. p. 76—77°. This reacts with sodium iodide to form the corresponding *iodo*-derivative, m. p. 116—118°, and with alcoholic ammonia at 50—60° to give the "*anhydride*" of 3 : 5-*diacetyl*-2 : 6-*dimethyl*-4-*aminomethylpyridine*, $\begin{array}{l}\text{CMe}\cdot\text{CAc:C—CH}_2\\ \text{N}\cdot\text{CMe}=\!=\text{C}\cdot\text{CMe}\end{array}\!\!>\!\text{N}$, which crystallises in dark reddish-brown needles, decomp. above 136°.

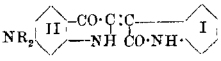
Benzoylacetonamine yields 3 : 5-*dibenzoyl*-2 : 6-*dimethyl*-4-*chloromethyl*-1 : 4-*dihydropyridine*, in sulphur-yellow needles, m. p. 183°, which forms a *nitro*-derivative, m. p. 168—169°, instead of suffering oxidation, when treated with nitric acid. J. C. W.

The Isatins which contain a Quinoleic Nucleus. J. Martinet (*Compt. rend.*, 1918, **166**, 998—1000).—Tetrahydroquinoline is converted by the action of ethyl mesoxalate into ethyl 1 : 7-trimethylenedioxindole-3-carboxylate, m. p. 174° (compare A., 1913, i, 756). In the same way, the author has prepared *ethyl* 5-*methyl*-1 : 7-*trimethylenedioxindole*-3-*carboxylate*, m. p. 162°, and *ethyl* 5-*methyl*-1 : 7-α-*methyltrimethylenedioxindole*-3-*carboxylate* (annexed formula), m. p. 108°. These esters when hydrolysed by alkalis and the product acidified give the corresponding isatins, which yield salts of the intermediate, unstable isatoic acids. Thus 1 : 7-*trimethyleneisatin*, red needles, m. p. 195°, giving a *phenylhydrazone*, m. p. 150°, yields the *potassium*, *copper*, and *lead* salts of 1 : 7-trimethyleneisatoic acid; 5-*methyl*-1 : 7-*trimethyleneisatin*, m. p. 185°, gives a *phenylhydrazone*, m. p. 177°, and yields *potassium* and *copper* 5-*methyl*-1 : 7-*trimethyleneisatoates*; 5-*methyl*-1 : 7-α-*methyltrimethyleneisatin*, m. p. 165°,



gives a *phenylhydrazone*, m. p. 141°, and the *barium* salt of the corresponding isatoic acid. The isatins when treated with hydrocyanic acid and the cyano-compound hydrolysed with hydrogen chloride in alcoholic solution are reconverted into the dioxindole-3-carboxylic esters. W. G.

Yellowish-brown Vat Dyes. SYNTHETIC PATENTS CO., NEW YORK (U.S. Pat. 1266092).—The new vat-dyes are compounds of the type



in which the benzene nucleus, I, contains halogen, the nucleus, II, may contain halogen, and R may be oxygen or hydrogen. As an example, the *compound* produced by the interaction of 5:7-dichloroisatin and 6-aminoindoxyl is cited; this is a dark brown, lustrous, crystalline powder, soluble in concentrated sulphuric acid with reddish-violet colour, which dyes cotton from the alkaline hyposulphite vat in yellowish-brown shades, fast to washing, light, and chlorine. J. C. W.

Alloxan and Alloxantin. EINAR BIILMANN and JOHANNE BENTZON (*Ber.*, 1918, **51**, 522—532).—Thunberg has recently shown that the solubility of alloxantin in water is greatly depressed by the addition of alloxan, and suggests, therefore, that alloxantin is the alloxan salt of dialuric acid (A., 1916, i, 635). Some careful determinations of these solubilities have now been made, and the results show that the solubility of alloxantin in the presence of alloxan obeys the mass law, and that it is possible to calculate the dissociation constant for alloxantin.

According to Richter's oxonium formula (A., 1911, i, 757), which is favoured by Thunberg, the dissociated particles would be an alloxan cation and a dialuric anion. Alloxan might be expected, therefore, to give the same cation in contact with hydrochloric acid, and consequently raise the freezing point of the acid, but in reality it has no such influence. Furthermore, solutions of alloxan become distinctly yellow on heating, but colourless again on cooling, owing to the formation and hydrolysis of the anhydride (Biltz, A., 1913, i, 166). This shows that alloxan is very susceptible to hydroxyl compounds, and excludes a quinonoid configuration for both alloxan and alloxantin. In fact, the arguments advanced are in favour of the formula

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(OH)\cdot O\cdot CH<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

for alloxantin. This "alcoholate" formula was first proposed by Slimmer and Stieglitz (A., 1904, i, 634).

The solubility determinations were carried out in an atmosphere

of carbon dioxide or nitrogen, the apparatus being described. Alloxantin was determined by titration with a solution of iodine in potassium iodide, and alloxan + alloxantin found from the result of a Kjeldahl estimation. The solubility of alloxantin, $C_8H_6O_8N_4,2H_2O$, in water at 25° is 0·2885 gram per 100 c.c. (or grams), of which about 22% is undissociated. The mean value of *K* at 25° = 38·7. J. C. W.

The Action of Hydrazine Hydrate on Cyanotetrazole. I. LIFSCHITZ and W. F. DONATH (*Rec. trav. chim.*, 1918, **37**, 270—293).—A more detailed account of work already published (compare A., 1915, i, 465; 1916, i, 436), and an elaboration of the work of Curtius, Darapsky, and Müller (compare A., 1916, i, 84) in reply to these authors.

When the mixture obtained by passing cyanogen into aqueous azoimide is treated with hydrazine hydrate, in addition to the *bishydrazonium salt of bistetrazole, there is obtained the hydrazonium* salt of *tetrazolecarbohydrazidine*,

$$N_2H_4{\cdot}CN_4H{\cdot}C{<}^{NH_2}_{N{\cdot}NH_2}$$

or $N_2H_4{\cdot}CN_4H{\cdot}C{<}^{NH}_{NH{\cdot}NH_2}$, m. p. 276°, which gives a *silver* salt, and when treated with nitrous acid yields bistetrazole. The hydrazonium salt when treated with aldehydes gives condensation products having the general composition $CHR{:}C_2H_3N_7$. Thus benzaldehyde gives a *compound*, m. p. 248°; anisaldehyde a *compound*, m. p. 252°; and *p*-nitrobenzaldehyde a *compound*, m. p. 240°.

The authors describe an *ethyl* derivative of ditetrazyldihydrotetrazine and an *ethyl* derivative of ditetrazyltetrazine. W. G.

Diazotisation of Nitrosobenzene. EUG. BAMBERGER (*Ber.*, 1918, **51**, 634—636).—Nitrosobenzene may be almost completely converted into a benzenediazonium salt by adding a very concentrated solution of sodium nitrite to a solution in cold acetic acid, or by means of amyl nitrite. The question is raised, which is the active agent, nitrous acid, nitrogen peroxide, or nitric oxide? No answer is given in the case of nitrous acid, but it has now been proved that dry nitrogen peroxide has no diazotising action, its only effect being that of an oxidising agent. Nitric oxide was shown some twenty years ago to convert nitrosobenzene into benzenediazonium nitrate. J. C. W.

Action of Di-*p*-diazo-*m*-tolylmethane Chloride on Naphthol- and Naphthylamine-sulphonic Acids. I. JAMES H. STEBBINS, jun. (*J. Ind. Eng. Chem.*, 1918, **10**, 445—448).—When *o*-toluidine is dissolved in dilute hydrochloric acid, mixed with formaldehyde, and kept at 70—76° for four hours, *di-*p*-aminodi-*m*-tolylmethane*, $C_6H_2(C_6H_3Me{\cdot}NH_2)_2$, *is obtained; it crystallises in rhombic prisms*, m. p. 149°. When this is diazotised, it yields *di-p-diazo-m-tolyl-*

methane chloride, $CH_2(C_6H_3Me\cdot N_2Cl)_2$. On mixing the diazotised solution with sodium α-naphthol-4-sulphonate, a copious, blood-red precipitate is obtained which seems to have the composition $\overset{4}{N_2Cl}\cdot C_6\overset{3}{H_3}\overset{1}{Me}\cdot CH_2\cdot C_6\overset{3}{H_3}\overset{4}{Me}\cdot \overset{7}{N_2}\cdot C_{10}\overset{1}{H_5}(OH)\cdot \overset{4}{SO_3H}$, and is gradually transformed into

$$OH\cdot C_6H_3Me\cdot CH_2\cdot C_6H_3Me\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3H.$$

The *sodium* and *barium* salts of the latter acid were prepared. In the presence of alcohol, two molecules of the naphtholsulphonic acid combine with the diazo-compound, and a heavy, carmine precipitate of the sodium salt of the acid,

$$CH_2[C_6H_3Me\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3H]_2,$$

is formed. The diazotised solution when mixed with an aqueous sodium carbonate solution of β-naphthol-3 : 6-disulphonic acid, yields a scarlet-red precipitate of the salt,

$$CH_2[C_6H_3Me\cdot N_2\cdot C_{10}H_4(SO_3Na)_2\cdot OH]_2.$$

W. P. S.

Nucleic Acid and its Analytical Examination. A. CHASTON CHAPMAN (*Analyst*, 1918, **43**, 259—263).—The chief difficulties in the preparation of pure nucleic acid are the complete removal of proteins and the prevention of the acid becoming contaminated with its own products of decomposition. Hydrolysis must therefore be effected under definite conditions. It is uncertain whether all nucleic acids are identical with one or other of the two typical nucleic acids obtained from yeast and from the thymus gland, but in practice yeast-nucleic acid is frequently described as "plant nucleic acid." Its chief products of hydrolysis are: guanine, adenine, cytosine, uracil, *d*-ribose (pentose), and phosphoric acid. Nucleic acid of animal origin, when hydrolysed, yields: guanine, adenine, cytosine, thymine, lævulic acid (from a hexose), and phosphoric acid. Plant nucleic acid is a white, friable, odourless substance with the formula $C_{38}H_{50}O_{29}N_{15}P_4$. It is nearly insoluble in water, but is readily soluble in solutions of alkali acetates, from which hydrochloric acid precipitates it as a curd-like precipitate soluble in excess of the acid. It forms characteristic salts with copper, calcium, and silver, and a strong aqueous solution of sodium nucleate gelatinises. It may also be identified by yielding guanine and adenine as distinctive products of hydrolysis. [See, further, *J. Soc. Chem. Ind.*, 1918, 441A.] C. A. M.

The Nature of the Aqueous Medium in the Enzymic Hydrolysis of Oils. Y. TANAKA (*J. Chem. Ind., Tokyo*, 1918, **21**, 112—117).—Referring to the experiments by Kita (A., 1918, i, 274), the author suggests that he was working with a lipase preparation still containing zymogen not completely activated by the previous treatment with acid, and consequently subject to a further stimulation when allowed to act on fats in an acidified medium. Further experiments have been made according to the author's method, by triturating pressed castor beans with eight

times their weight of $N/10$-acetic acid, washing, and drying the insoluble residue. A series of hydrolyses was carried out with 2 grams of the activated lipase powder and 25 grams each of soja bean oil at 38—39°, in 10 c.c. of aqueous substratum, containing increasing amounts of $N/10$-sulphuric acid. The percentage of oil hydrolysed in one hour decreased with increasing acidity of the medium, thus: with 0·0 c.c. acid, 58·4%; 0·5 c.c., 53·8%; 1·0 c.c., 51·2%; 2·0 c.c., 40·0%. The results after five hours were in the same order. Thus it is confirmed that castor bean lipase which has been treated with the optimum quantity of acid and washed acts most energetically in neutral media. J. F. B.

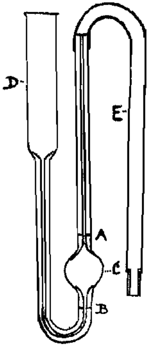
Action of Ethyl Alcohol and Acetone on Lipase. GEN-ITSU KITA and MINORU OSUMI (*J. Tokyo Chem. Soc.*, 1918, **39**, 13—22). —Connstein, Hoyer, and Wartenburg (A., 1903, i, 218), Hoyer (A., 1907, ii, 192), and Falk (A., 1913, i, 664) have already observed that the activity of lipase is destroyed by ethyl alcohol. The author has repeated this investigation, and finds that when the activity of lipase has been destroyed by alcohol, it cannot be restored by any treatment. Contrary to the statements of Hoyer and Falk, acetone has no particular influence on the activity. S. H.

Physiological Chemistry.

Transport of Carbon Dioxide by Solutions of Sodium Hydrogen Carbonate. G. A. BUCKMASTER (*Proc. physiol. Soc.*, 1918, xvi—xvii; *J. Physiol.*, **52**; from *Physiol. Abstr.*, 1918, **3**, 177).—The dissociation tensions of solutions of varying quantities of pure sodium hydrogen carbonate in boiled-out water were determined at 38° in an atmosphere of air, nitrogen, and a mixture of nitrogen and carbon dioxide respectively. The average dissociation tension was 2·25 mm. of mercury in air and carbon dioxide respectively. In a mixture of nitrogen and carbon dioxide, with tensions of the latter within the range of alveolar air, there was no dissociation and carbon dioxide was actually absorbed, and it is therefore improbable that the transport of carbon dioxide in the blood is a function of the sodium carbonate. S. B. S.

***Viscosity of Blood.** J. W. TREVAN (*Biochem. J.*, 1918, **12**, 60—71).—The viscosimeter is blown from glass tubing of 0·8 mm. diameter for the large size, using 2 c.c. of blood, and 0·2 mm. diameter for the small form requiring only 1 c.c. of blood. In the large model, the bulb, *C* (see Fig.), holds rather less than 1 c.c.; the other dimensions are in proportion. The funnel, *D*, is made from a test-tube (1·25 cm.) drawn out and fused on, and holds about

5 c.c. The blood is mixed with a little hirudin in D and allowed to run into C. The instrument is then placed in a thermostat at 40° for ten minutes. The bulb, C, is then emptied into D by slowly blowing down the rubber tube, E, until the whole of the blood is in D. The corpuscles are mixed with the plasma by stirring with a coiled wire, and then the blood is allowed to flow back again into C, the time of flow from B to A being noted with a stop-watch, and the blood in D being stirred continually with the coiled wire.



The results show that the viscosity of the blood is directly proportional to that of the plasma over a very wide range of plasma viscosity provided the volume of corpuscles remains constant. Any increase in the number of corpuscles greatly increases the viscosity of the blood. The relation is expressed by the formula $100/P=(n/n-1)^3$, where P is the percentage volume of corpuscles in the blood and n is the ratio of the viscosity of the whole blood to that of the plasma. The bearing of the results on the interpretation of certain phenomena associated with inflammation, infarction, and blood circulation generally are discussed.

H. W. B.

Physiology of Blood-sugar. II. Lépine's "Sucre virtuel." RICHARD EGE (*Biochem. Zeitsch.*, 1918, **87**, 92—103).—According to Lépine (numerous papers, 1902—1914), part of the sugar in blood is free ("sucre immedial"), whereas part is bound in chemical combination and only set free after hydrolysis ("sucre virtuel"). Using ferments and other treatment, the author has been unable to confirm Lépine's statement as to the existence of the two forms of blood-sugar.

S. B. S.

Influence of Morphine, and of Morphine with Ether Anæsthesia, on the Dextrose in the Blood. ELLISON L. ROSS (*J. Biol. Chem.*, 1918, **34**, 335—342).—The subcutaneous injection of morphine into a dog is followed by a pronounced glycosuria, which, although not so intense as that which may be produced by simple ether anæsthesia, is nevertheless increased by subsequent administration of ether, so that the final degree of hyperglycæmia reached is approximately the same, either with or without the preliminary morphine injection.

H. W. B.

Rate of Dialysis of the Dextrose in the Blood in Experimental Diabetes. ISRAEL S. KLEINER (*J. Biol. Chem.*, 1918, **34**, 471—487).—The rate of dialysis of dextrose from blood into Ringer's solution is dependent on the state of the animal from which the blood is obtained. The dextrose in the blood from a

diabetic animal dialyses at an irregular rate showing more or less completely arrested dialysis, usually about two hours after the commencement of the experiment. The dialysis of the dextrose in normal blood, to which dextrose has been added to bring it to the same dextrose content as the diabetic blood, occurs at a uniform rate. The author suggests that in diabetes the dextrose exists partly in a combined state in the blood, which tends to hinder its dialysis (compare Michaelis and Rona, A., 1909, ii, 68).

H. W. B.

Acetone Substances in the Blood in Diabetes. ERNEST LAURENCE KENNAWAY (*Biochem. J.*, 1918, **12**, 120—130).—The concentration of acetone substances in the blood in diabetic coma may be equivalent, when reckoned as acetoacetic acid, to that of a $0 \cdot 03N$-solution; this amount is sufficient to combine with more than one-third of the sodium of the plasma. H. W. B.

The Existence of Creatinine and Creatine in the Blood in Normal and Pathological Cases. III. Normal Cases, especially in Old Age. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **87**, 1—22).—The creatinine and creatine content in the blood of individuals of varying ages is tabulated according to the ages.

S. B. S.

The Presence of Phosphates in Human Blood-serum. VI. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **87**, 237—247).—A general summary of results dealing with the acid soluble and residual phosphorus in pathological cases, with the relationship between the lipoid and residual phosphorus, and with lecithinæmia in cases of mental diseases. S. B. S.

Chemical Studies in Physiology and Pathology. IV. Hæmolysis. The Complement. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **87**, 36—76. Compare this vol., i, 241). —The authors develop further their conceptions as to the chemical and physical nature of proteins and the mode of action of proteoclastic ferments.

Hæmolysis, according to their views, depends on the destruction of the semipermeable structure of the membrane of the blood-corpuscles. This can be brought about either by mechanical or chemical means. Included in the former are such methods as the sudden transference of the corpuscles to hyper- or hypo-tonic solution, drying, etc. The chemical hæmolytics act either directly as solvents (especially for the lipoid constituents) or they act as hydrolytic reagents on lipoids or proteins, or on both.

The agglutination of erythrocytes follows the same laws as that of bacteria and other "hydrophil" suspensions, and is connected intimately with the hydrophil capacity of the surfaces.

In the action of the complement, two functions are to be distinguished. (1) That of the "middle-piece," which is a globulin precipitation and renders the surface of the blood cells more capable

of taking up certain degradation products of the serum ("per-sensitisation") which form the constituents of the "end-piece." (2) The "end-piece" function consists in the direct solvent or hydrolytic action of the degradation products contained in the albumin fraction. The chief influences which inhibit or destroy the complement action can be ascribed to actions on the globulins, which render these substances too stable and less liable to be precipitated, such as dilution with water, Brand's modification, addition of citrates, oxalates, acids, alkalis, action of heat, etc. Other "anti-complement" actions consist in removal of the globulins from the serum, such as addition of precipitants of globulins, bacteria, agar, and cobra-poison. S. B. S.

Action of Symbiotic Bacteria on the Constituents of Fats. HENRI BIERRY and PAUL PORTIER (*Compt. rend.*, 1918, **166**, 1055—1057).—The symbiotic bacteria isolated from the testicle of a pigeon oxidise glycerol in a yeast bouillon, giving a C_3 sugar, glycerose, but the same organisms in a chemically definite medium containing asparagine, glycerol, nitrate, etc., give no trace of dihydroxyacetone. The symbiotes also cause β-oxidation, acetaldehyde and acetone being obtained from β-hydroxybutyric acid and from butyric acid. W. G.

Importance of the Ketonic Function in Metabolism. Its Creation by Symbiotic Bacteria. PAUL PORTIER and HENRI BIERRY (*Compt. rend.*, 1918, **167**, 94—96. Compare preceding abstract).—It is shown that the symbiotes of mammals and birds are capable, in suitable medium, of converting pentoses, hexoses, disaccharides, and certain polyhydric alcohols into acetylmethylcarbinol, amongst other products. On the other hand, when the conditions of the medium are suitable, they are capable of synthesising polysaccharides, the yield of the latter being greatest when a ketose is present. It is also noted that the production of a polysaccharide by symbiotic action is always accompanied by the production of alkalinity in the medium. W. G.

Sugar Metabolism and Diabetes. H. McGUIGAN (*J. Lab. and Clin. Med.*, 1918, **3**, 319—337; from *Physiol. Abstr.*, 1918, **3**, 182—183).—Attention is directed to the variations found in the reducing substances in the blood caused by differences in the concentration of the alkali, and of salts when the latter have been used for precipitating the proteins. There is apparently no difference in the condition of sugar in the blood in normal and in diabetic cases. Observations on utilisation of sugar in muscular contraction, on effect of vascular changes in the liver on glycogenolysis, and on peptone hypoglycæmia are recorded. S. B. S.

The Water-soluble Accessory Growth-promoting Substance. II. Its Influence on the Nutrition and Nitrogen Metabolism of the Rat. JACK CECIL DRUMMOND (*Biochem. J.*, 1918, **12**, 25—41).—When rats are fed on an artificial diet deficient

in the water-soluble accessory substance, the only apparent deviation from the normal nitrogen metabolism is the appearance of creatinuria, accompanied by a slow wasting of the skeletal muscles. The food consumption is low; it may be increased by the addition of flavouring agents, such as meat extract, to the diet, but unless this agent contains the water-soluble accessory, growth does not occur. The addition to the inadequate diet of extracts containing the water-soluble substance causes a greatly increased intake of food, immediately followed by growth. The amount of growth is, within certain limits, proportional to the amount of accessory substance added, provided that the diet is adequate in other respects. The length of time that a rat is able to maintain itself on a diet deficient in the water-soluble substance without suffering a serious loss of body-weight is directly proportional to the age at which the restriction is imposed. Actively growing animal tissues (embryos, tumours) do not contain appreciable amounts of the water-soluble accessory substance; desiccated pituitary, thyroid, and thymus glands, and testicular and ovarian tissues, are also deficient in this respect. H. W. B.

The Utilisation of Yeast in the Animal Organism. Emerich Schill (*Biochem. Zeitsch.*, 1918, **87**, 163—175).—Experiments on dogs indicated that the proteins of yeast can not only be resorbed by the organism, but can produce a positive nitrogen balance. About half the chemical energy of yeast can be utilised by the organism. S. B. S.

Influence of the Species of Animal on the Toxicity and Mode of Utilisation of Alimentary Proteins. E. Maignon (*Compt. rend.*, 1918, **167**, 91—94).—Feeding experiments, similar to those carried out with white rats, have been performed with dogs, the same three proteins (egg-albumin, fibrin, casein) being used. The dog accommodates itself much better than the rat to a purely protein diet, and was able to retain its weight for a considerable time on casein or meat powder alone. On the other hand, casein is much more toxic for dogs than for rats. Whereas rats on this diet died from exhaustion of their reserves, dogs died undoubtedly as a result of toxic action. The toxicity of a given protein varies from one species of animal to another apparently inversely as the ease with which the animal can transform the protein into fat. W. G.

Digestion of the Proteins of Cooked Meat in Dogs with Ligatured Carotid Arteries. Edgard Zunz (*Biochem. J.*, 1918, **12**, 42—59).—After the ligature of the carotids, a meat meal is retained in the stomach for a longer time than occurs in the normal animal, due, apparently, to an altered blood supply to, or innervation of, the stomach produced by the operation. H. W. B.

Origin of the Conception of Physiologically Balanced Salt Solutions. Jacques Loeb (*J. Biol. Chem.*, 1918, **34**, 503—504).—The author claims to have originated the conception

of physiologically balanced salt solutions (*Amer. J. Physiol.*, 1899—1900, **3**, 445). H. W. B.

Active Substances in Glands with Internal Secretions. ERNST BERLIN (*Zeitsch. Biol.*, 1918, **68**, 371—390).—Extracts of spleen contain, besides choline, a substance which exerts a powerful action on the muscles of the uterus and intestine. The latter substance is not β-amino-4-ethylglyoxaline. Both choline and the unknown substance occur also in a commercial extract of spleen called hormonal. H. W. B.

The Genesis of Thiocyanic Acid in Animals. S. DEZANI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 113—128; from *Physiol. Abstr.*, 1918, **3**, 164).—Thioacetamide does not give rise to thiocyanic acid in the dog, and thus the hypothesis of Röhmann as to its genesis from fatty nitriles through the corresponding thioamides or thioamidic acids is not substantiated. In the dog, the ingested nitrile is partly transformed into thiocyanic acid and partly eliminated as such. The remainder is transformed into products which have not yet been identified. S. B. S.

Anti-scorbutic Value of Cow's Milk. HARRIETTE CHICK, ELEANOR MARGARET HUME, and RUTH FILBY SKELTON (*Biochem. J.*, 1918, **12**, 131—153).—Guinea-pigs grow when fed on a diet of oats and bran with milk which has been heated at 120° under pressure, but they rapidly develop scurvy. If some fresh, unheated milk is added to the diet, scurvy may appear sooner or later, according to the amount of milk in the daily ration. By greatly increasing the amount of milk so that the daily ration exceeds 100 c.c., the onset of scurvy is entirely prevented. Milk is therefore relatively poor in the anti-scorbutic accessory substance, and it is most essential that, for the prevention of scurvy, infants fed on milk which has been previously heated or dried should also be given orange juice, raw swede juice, or similar material rich in the anti-scorbutic vitamine. A connexion between scurvy and chronic constipation (McCollum and Pitz, A., 1917, i, 604) is not confirmed. H. W. B.

Milk as a Source of Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 537—551).—The authors find that vigorous growth of rats does not occur on diets in which the water-soluble vitamine is supplied by milk unless considerable quantities of the milk are consumed. Milk does not contain, therefore, as much water-soluble vitamine as Hopkins's experiments (A., 1912, ii, 779) would lead one to expect (compare preceding abstract). H. W. B.

Carbon Dioxide Content of Urine. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1918, **34**, 569—575).—The total amount

of free and combined carbon dioxide passed in the urine in twenty-four hours by a normal person may vary from 4 to 400 c.c., according to the nature of the ingested food. Vegetable food increases and animal food decreases the output of carbon dioxide in the urine. The carbon dioxide present in the urine varies inversely, although not proportionately, with the hydrogen ion concentration.

H. W. B.

Creatine and Creatinine. VIII. Alleged Exogenous Origin of Urinary Creatine in the Protein of the Diet. WILLIAM C. ROSE, J. STERLING DIMMITT, and H. LEIGH BARTLETT (*J. Biol. Chem.*, 1918, **34**, 601—612).—The authors find that the ingestion of diets excessively high in protein fails to induce the excretion of creatine in normal men and women. The theory that creatine has an exogenous origin in the protein of the diet is not confirmed (compare Denis, Kramer, and Minot, A., 1917, i, 526).

H. W. B.

Examination of the Fæces of Rabbits Fed on a Diet of Cabbage for the Occurrence of a Phytosterol. The Phytosterols in Cabbage Seeds and Grass Fruits. MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 154—159).—The fæces of rabbits fed on cabbage do not contain a typical phytosterol, but a trace of a substance resembling coprosterol, melting at 102°, may be detected. Cabbage seeds contain a relatively large amount of phytosterols similar to those present in rape oil. Grass fruits contain a trace of phytosterol, together with chortosterol (compare Dorée and Gardner, A., 1908, ii, 514). H. W. B.

Biochemistry and Chemotherapy of Tuberculosis. XVI. Pharmacology and Toxicology of Copper Salts of Amino-acids. HARRY L. HUBER (*J. Pharm. Exp. Ther.*, 1918, **11**, 303—329).—The copper salts of leucine, glycine, and glutamic acid produce exactly the same physiological effects as copper sulphate when administered in various ways to guinea-pigs and rabbits.

H. W. B.

Effect of Intravenous Injections of some Sodium Salts with Special Reference to the supposed Toxicity of Sodium Phosphate. ISIDOR GREENWALD (*J. Pharm. Exp. Ther.*, 1918, **11**, 281—301).—The intravenous injection of neutral solutions of sodium chloride, sulphate, and phosphate into dogs produces changes in the volume, osmotic pressure, and reaction of the blood, and results in disturbances of the normal relations between the various ions of the blood and tissues. It is to these physical factors rather than to a direct toxic action of the phosphate ion that the ill-effects observed after the administration of sodium phosphate solutions are to be ascribed (compare Binger, A., 1917, i, 677). Muscle twitching, tetany, and violent convulsions may be produced by the injection of the chloride and sulphate, as well as of the

phosphate of sodium, and seem to be dependent more on the sodium than on the phosphate ion, since a balanced solution containing high concentrations of sodium, potassium, and calcium in certain fixed proportions may be introduced without producing any ill-effects. The injection of sodium salts is followed by the elimination of both potassium and calcium salts in the urine, but whereas the content of calcium in the blood and serum falls, that of potassium remains unchanged. Similarly, the injection of either sodium sulphate or phosphate, as well as of the chloride, occasions an increased elimination of chlorides in the urine, probably due to differences in the permeability of the kidneys to the different salts. H. W. B.

Metabolism of the Mustard Oils. W. H. PETERSON (*J. Biol. Chem.*, 1918, **34**, 583—600).—The addition of allylthiocarbimide, 0·2 to 0·4 gram per day, and allyl sulphide, 0·5 to 1 gram per day, to the starchy diet of a pig produces a gradual rise in the total sulphur excreted in the urine, which persists for ten to twelve days after the ingestion of these compounds has ceased. This points to a very slow metabolism and the inability of the body to dispose readily of them. These compounds are not oxidised during their passage through the body, but are converted into a non-volatile, less toxic substance which has not been identified. From 40 to 70% of the sulphur in the ingested compound can be subsequently recovered from the urine, the remainder being probably eliminated in the form of volatile compounds through the lungs and skin. The two sulphur compounds are practically completely absorbed, scarcely a trace being excreted in the fæces.

H. W. B.

The Behaviour of Urotropine and Formaldehyde in the Organism. E. SALKOWSKI (*Biochem. Zeitsch.*, 1918, **87**, 143—162).—The author has investigated the various reactions for formaldehyde with the object of detecting this substance in the presence of much larger quantities of urotropine. The only quite satisfactory reaction for this purpose was found to be that of Jorissen as modified by Vanino (with phloroglucinol and sodium hydroxide. A., 1899, ii, 703). Solutions of urotropine cannot be kept without decomposition for any great length of time; they are somewhat more stable in the presence of sodium carbonate (0·1—1%), and such solutions can be kept without appreciable change for a week. In the presence of slight amounts of acid, solutious alter from day to day. There is, apparently, a scission of formaldehyde from urotropine, which takes place in the stomach. Examination of the urine after ingestion of urotropine reveals the fact that it is partly excreted unchanged, and partly oxidised to formic acid.

S. B. S.

Atophan and some of its Derivatives. LOISE ROTTER (*Zeitsch. exp. Path. Ther.*, 1917, **19**, 176—197; from *Physiol. Abstr.*, 1918, **3**, 194—195).—Atophan (2-phenylcinchonic acid) is

toxic to cold-blooded, but not to warm-blooded animals. It paralyses both the central nervous system and the nerves of the heart of frogs, and the heart generally stops beating in systole. Atophan owes its activity to the linking up of a phenyl group to a quinoline nucleus, as quinolinecarboxylic acid is almost inactive. Other substitution products were investigated, and generalisations as to chemical constitution and pharmacological action are made. No substance antagonistic in action to atophan was discovered. After ingestion by the mouth in man, hydroxyphenylquinolinecarboxylic acid is excreted in the urine, together with an increased amount of uric acid. To the former the increased output of uric acid is ascribed, as such an increased excretion can be produced by its direct administration. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Action of Cyanohydrins on Ferments and Bacteria. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **87**, 129—134).—The action of the urease of soya bean is strengthened by the presence of the cyanohydrin of acetaldehyde, but inhibited by the corresponding propaldehyde derivative. Both compounds inhibit strongly the ferment formation by bacteria, whilst they exert only a very moderate deleterious action on the bacteria themselves.

S. B. S.

The Degradation of Tyrosine by Bacterium coli phenologenes, and the Composition of Human Urines containing Phenol. M. RHEIN (*Biochem. Zeitsch.*, 1918, **87**, 123—128).—Phenol is formed by *Bacterium coli phenologenes* only from tyrosine and *p*-hydroxybenzoic acid. It was not formed from the following (possible intermediary degradation products of tyrosine): *p*-hydroxyphenylpropionic acid, *p*-hydroxyphenylacetic acid, *p*-hydroxyphenylpyruvic acid, *p*-hydroxyphenylethylamine, *p*-hydroxyphenylethyl- alcohol, *p*-hydroxyphenyl-α-lactic acid, and *p*-cresol. It appears, therefore, that tyrosine is degraded by attack of the β-carbon atom of the alanine chain and simultaneous oxidation. Phenol and *p*-cresol in human urines can be detected readily by the colour reactions with formaldehyde–sulphuric acid and with diazobenzenesulphonic acid in sodium carbonate solutions.

S. B. S.

The Influence of Lactic Acid on Lactic Acid Fermentation. W. VAN DAM (*Biochem. Zeitsch.*, 1918, **87**, 107—122).—Investigations were made to ascertain whether the stoppage of fermentation by the coccal form of bacteria is due to the action of the hydrion

of the lactic acid produced or to the undissociated molecule. The conclusion is drawn that the stoppage is due to both. If sodium lactate is added to the whey, further acid formation ceases when the concentration of the undissociated molecule reaches 0·01*N*. In such cases, the final hydrion concentration fails to reach the toxic amount of about 10×10^{-5}. If hydrochloric acid is added to the whey before inoculation, so much lactic acid is formed as to bring the final hydrion concentration to $10—20 \times 10^{-5}N$. In this case, the amount of undissociated lactate remains below the toxic amount. Attention is directed to the fact that certain conclusions of other authors as to the value of the nitrogenous nutrients are vitiated by their failing to take into account their buffer action.

S. B. S.

The Bacterial Degradation of *d*-Tyrosine, with Special Reference to the Stereochemical Configuration of the Degradation Products. M. Tsudji (*Acta. Schol. Med. Kyoto*, 1918, **2**, 115—123; from *Physiol. Abstr.*, 1918, **3**, 165).—A continuation of previous work (A., 1917, i, 679). Although in degradation of the *dl*-form, the *l*-form is rapidly acted on, the *d*-form does not remain entirely intact, and can be slowly broken down by *Bacterium subtilis* or *B. proteus* in media containing phosphates. The same products are obtained whether *dl*-, *d*-, or *l*-tyrosine is used as substrate, namely, *d*-*p*-hydroxyphenyllactic acid by the action of *B. proteus* and the corresponding *l*-acid by the action of *B. subtilis*. It is suggested that in both cases the inactive *p*-hydroxyphenylpyruvic acid is formed as an intermediate product.

S. B. S.

By-products of the Fermentation of Cabbage. V. E. Nelson and A. J. Beck (*J. Amer. Chem. Soc.*, 1918, **40**, 1001—1005).—The fermented cabbage examined was the ordinary commercial material, "sauerkraut." The volatile acidity represented from 25—50% of the total acidity. The volatile acids consisted of acetic and propionic acids, no higher acids being present, although in two cases formic acid was isolated. The fixed acidity was in all probability due to an inactive form of lactic acid. Alcohols were present to the same extent as volatile acids, and consisted entirely of ethyl and propyl alcohols. Esters, present only in small amount, contributed an essential part in the flavour and aroma. Mannitol was present in the fermented cabbage to the extent of 2·0—2·5%, and must have arisen from bacterial decomposition of the carbohydrates, since none is present in the natural plant.

W. G.

Formation of Esters of Phosphoric Acid during Alcoholic Fermentation. Alexandre Lebedev (*Biochem. J.*, 1918, **12**, 87—92).—By treatment of a fermenting solution containing yeast, sucrose, and phosphates with alcohol, a mixture of esters of phosphoric acid can be isolated which yields an *osazone*, $C_{33}H_{37}O_7N_8P$;

his appears to be the osazone of an ester of phosphoric acid containing one molecule of the latter combined with a molecule of hexose and a molecule of triose. The osazone or mixture of osazones melts at 142—144°; a p-*bromophenylosazone*, m. p. 141—142°, and a *barium* salt have also been isolated, and in each case have been found to possess different properties from those associated with the corresponding compounds of ordinary hexose phosphate.

H. W. B.

Fermentation of Glyoxylic Acid. ALEXANDRE LEBEDEV (*Biochem. J.*, 1918, **12**, 81—86).—Dried yeast (Lebedev) decomposes glyoxylic acid, forming carbon dioxide and acetaldehyde.

H. W. B.

Nature of the Proteolytic Enzyme of Yeast. NICOLAUS IVANOV (*Biochem. J.*, 1918, **12**, 106—119).—When autolysing yeast is treated with potassium hydrogen phosphate, the decomposition of protein is accelerated, resulting in an increased production of peptones. A similar accumulation of peptones occurs when the autolysis proceeds at a relatively high temperature (54°). If, however, the autolysis proceeds in an alkaline medium, the decomposition of the proteins is inhibited, whilst a large production of amino-acids is obtained. Apparently the proteolytic enzyme of yeast is composed of two factors, a protease acting on proteins and forming peptones, and a peptase transforming the peptones into amino-acids. By varying the conditions in the manner indicated above, it is possible to inhibit the action of one factor without interfering with the activity of the other. It is probable that the peptase of yeast is identical with animal erepsin. H. W. B.

Differential Behaviour of the Antineuritic and Antiscorbutic Factors towards Adsorbents. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 93—105).—The anti-neuritic substance present in autolysed yeast is quantitatively adsorbed by fuller's earth or by dialysed iron. When a mixture of equal volumes of autolysed yeast (containing the anti-neuritic factor) and orange juice (containing the anti-scorbutic factor) is treated with fuller's earth, the anti-neuritic factor is entirely removed, whilst the anti-scorbutic activity remains unaltered. So far, it has not been found possible to separate the anti-neuritic substance in an active form from the fuller's earth adsorption complex. H. W. B.

The Formation of Nitrites from Nitrates in Aqueous Solution by the Action of Sunlight and the Assimilation of the Nitrites by Green Leaves in Sunlight. BENJAMIN MOORE (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 158—167).—Dilute solutions of nitrates exposed either to sunlight or to a light-source rich in light energy undergo conversion into nitrites. If leaves are immersed in the nitrate solutions, comparatively little nitrite accumulates.

Nitrates taken up by plants from soil would, in the presence of sunlight, be converted into nitrites, which are more reactive, and it is held by the author that the early stages of synthesis of nitrogenous compounds are carried out by the green leaf, aided by sunlight. Rain-water collected for a considerable time contains no nitrites, all having been oxidised to nitrates, but if exposed to light for a few hours, a strong reaction for nitrites is obtained. Freshly-collected rain-water or dew contains both nitrates and nitrites. Air bubbled through nitrite- and nitrate-free water gives a reaction, when the water is tested afterwards for nitrates and nitrites showing the presence of both forms of oxides of nitrogen in air. The "ozone" odour in air is probably due to oxides of nitrogen formed by the action of sunlight rich in ultra-violet light in the upper layers of the atmosphere on air and water-vapour. S. B. S.

The Carbohydrate Nutrition of Plants. T. Bokorny (*Biol. Zentr.*, 1916, **36**, 385—403; from *Physiol. Abstr.*, 1918, **3**, 208). —De-starched *Spirogyra* in water free from carbon dioxide can form starch in light from lactose, galactose, raffinose, dextrose, methyl alcohol, glycerol, ethyl acetate in the presence of monohydrogen dipotassium phosphate, and formaldehyde. It does not form starch under similar conditions from lævulose, sorbose, arabinose, xylose, rhamnose, acetone, and a number of other organic substances. Yeasts can apparently use methyl alcohol as a source of carbon only in the presence of dextrose or sucrose. S. B. S.

Metachromatin and the Phenolic Compounds of the Plant Cell. A. Guilliermond (*Compt. rend.*, 1918, **166**, 958—960). —The substance existing in the higher plants described by Dangeard as metachromatin is not comparable with the metachromatin of fungi. It is a phenolic compound capable of being converted into anthocyanin, which is formed thus by a chemical transformation of this compound, and not by fixation on it. The presence of this compound in the vacuole is not general, only being localised in special tissues. W. G.

The Constitution of a Plant Salt coming from the Cameroons. A. Lacroix (*Compt. rend.*, 1918, **166**, 1013—1015. Compare Dybowski and Demoussy, *ibid.*, 1893, **116**, 398).—The salt is obtained by lixiviation of the plant ashes of a grass, which is probably *Panicum crus Galli*, L. Its principal ingredients are: Cl=42·81%; SO_3, 5·24%; K_2O, 56·73%; Na_2O, 1·63%; CaO, 1·19%, and a little magnesia, silica, and organic matter. Mineralogically, it is found to contain sylvine, sodium chloride, magnesium chloride, syngenite, and glaserite. W. G.

Transformation of Inulenin by Autohydrolysis in the Tubercles of Asphodels. E. Couvreur (*Compt. rend. soc. biol.*, 1918, **81**, 40—41; from *Physiol. Abstr.*, 1918, **3**, 201).—Inulenin differs from inulin in its mode of crystallisation in fine needles. Maltose is not present in the tubercles of the fresh tissues of

Asphodel crassiferus and *A. microcarpus*, but appears after they have been triturated with water, and can be identified by the osazone test. S. B. S.

Chemistry of the Cotton Plant, with Special Reference to Upland Cotton. ARNO VIEHOEVER, LEWIS H. CHERNOFF, and CARL O. JOHNS (*J. Agric. Research*, 1918, **13**, 345—352. Compare Perkin, T., 1909, **95**, 1855, 2181; 1916, **109**, 145).—Quercimeritrin and *iso*quercitrin, previously isolated by Perkin (*loc. cit.*) from other types of cotton plant, have now been found in Upland cotton (*Gossypium hirsutum*). The leaves and flowers, with petals removed, contain quercimeritrin, whilst the petals contain this and *iso*quercitrin. Gossypitrin and gossypetin, which have been isolated from other types of cotton, could not be found in Upland cotton. The authors also isolated an ethereal oil from *G. hirsutum* differing from that found by Power and Browning (compare A., 1914, i, 1163) in the root bark of *G. herbaceum*. The new oil, present only to the extent of 0·0015 to 0·0071%, distils mainly between 200° and 300°, and leaves a black, empyreumatic residue; it is attractive to the boll weevil. W. G.

Chemistry and Histology of the Glands of the Cotton Plant, with Notes on the Occurrence of Similar Glands in Related Plants. ERNEST E. STANFORD and ARNO VIEHOEVER (*J. Agric. Research*, 1918, **13**, 419—436).—For the most part botanical. The glands in portions of the plant which are exposed to light are surrounded by an anthocyanin-bearing envelope of flattened cells, and contain quercetin, probably partly or wholly in the form of its glucosides, quercimeritrin or *iso*quercitrin, ethereal oils, resins, and perhaps tannins. The glands not normally exposed to light contain gossypol, and are surrounded by cells not containing anthocyanins. Gossypol is formed in the glands of the developing corolla, and on their exposure to light it is replaced by quercimeritrin. In the unfolding cotyledons, gossypol is changed, probably through oxidation, without the formation of quercimeritrin. W. G.

The Active Glucosides of Digitalis Leaves of Various Origin and some Commercial Galenicals Compared Quantitatively. ERNST MEYER (*Arch. exp. Path. Pharm.*, 1917, **81**, 261—288).—Kraft's gitalin (A., 1911, i, 734; 1912, i, 373) is very readily soluble in chloroform, but not in water; yet it cannot be extracted by chloroform from perfectly dry leaves, or from a cold water leaf-extract which has been completely dried over sulphuric acid. The addition of very little water to the dried extract, however, again renders the gitalin soluble in chloroform, and hence it can also be extracted from fresh leaves by chloroform. The extraction of gitalin from the leaves by cold water is attributed to the presence of tannins (see following abstract), from which the gitalin may be separated by chloroform.

Of commercial preparations, digalen and its copy digipan contain gitalin, and are probably cold water extracts. Digipuratum and digitalysatum contain only a portion of the gitalin and correspond with hot water infusions. G. B.

The Amount of Substances with a Digitalis Action in Oleander Leaves and the manner of their Natural Occurrence (Tannoid Question). WALTHER STRAUB (*Arch. exp. Path. Pharm.*, 1918, **82**, 327—343).—The activity of oleander leaves is about 2·5 times as great as that of digitalis leaves. Two crystalline active glucosides have been obtained by Böhringer & Söhne. One of these, *oleandrin* (C 67·85%, H 7·74%), is very active, about as much so as amorphous *k*-strophantin, and is almost insoluble in water when pure. Amorphous active glucosides are also present in larger amount. Nevertheless, the whole of the active snbstances are readily extracted by cold water, and this solubility seems due to the large amount of a phenolic glucoside present in the leaves, which is not a true tannin. This substance is coloured green by ferric chloride, and is also present in digitalis leaves, but in smaller amount, so that the whole of the active substances of digitalis are *not extracted by cold water.* (*See preceding abstract.*) G. B.

Action of Normal Salts on Humus and other Experiments on Soil Acidity. LOUIS J. GILLESPIE and LOUIS E. WISE (*J. Amer. Chem. Soc.*, 1918, **40**, 796—812. Compare Gillespie, A., 1916, i. 303; Sharp and Hoagland, *J. Agric. Research*, 1916, **7**, 123).—The addition of solutions of chloride of sodinm, potassium, or barium to humus causes a large increase in the hydrogen ion concentration as measured electrometrically, but as similar although smaller effects are observable in the action of potassium chloride on true solutions in the absence of humus or of undissolved solid matter, great care is required in drawing conclusions as to the mechanism of the process in the case of humus. At equivalent concentrations, barium chloride exerted the greatest influence on the electrometric potential of humus preparations. Considerable precaution is necessary in using litmus for the detection of acidity of soils, because even in very dilute solutions of hydrochloric acid the result is largely influenced by the "buffer" action of the solution under test. It is improbable that soils can act on litmus solely by virtue of their adsorptive power, and the difference in the effect of a moistened soil and of its aqueous extract on litmus may be due to the sparing solubility of the acidic organic substances of the soil. It is inadvisable at present to attempt broad general explanations of the cause of soil acidity, but the investigations with the hydrogen electrode and snitable indicators supply ample evidence of the common occurrence and wide distribution of truly acid soils in the United States. D. F. T.

Organic Chemistry.

Nature of the Kolbe Electrochemical Synthesis of Hydrocarbons. FR. FICHTER and EDUARD KRUMMENACHER (*Helvetica Chim. Acta*, 1918, **1**, 146—166).—The authors discuss the two theories put forward to explain the mechanism of the Kolbe hydrocarbon synthesis, and draw the conclusion that the oxidation theory is more in accord with fact than the theory based on the ionic hypothesis. It is shown that peroxides are produced by electrochemical oxidation, on platinum anodes, of solutions of saturated fatty acids and their salts. Since these peroxides may be produced by the action of hydrogen peroxide on acid anhydrides, it is to be assumed that the separation of the anhydride is the first step in the hydrocarbon synthesis. The anhydride is then anodically oxidised, with the formation of a very unstable peroxide. The peroxide is then decomposed by the relatively high temperature of the anode, with the formation of the hydrocarbon, thus: $R\cdot CO_2Na \longrightarrow (RCO)_2\cdot O + O \longrightarrow (RCO)_2\cdot O{=}O \longrightarrow R\cdot R + 2CO_2$, or a side reaction may also occur, thus: $(R\cdot CO)_2O{=}O \longrightarrow R\cdot CO_2\cdot R + CO_2$. When the peroxides are decomposed by heat, there is also a considerable amount of methane produced in addition to the expected hydrocarbon.

These considerations are adapted to the formation and decomposition of organic peracids. Organic peracids may be prepared by the action of hydrogen peroxide on both acids and anhydrides, consequently the formation of these substances electrolytically on the anode does not necessarily demand the intermediary formation of the anhydride. A further possibility also arises from the fact that peracids may be hydrolysed to peroxides. The peracids also decompose at the anode surface, giving carbon dioxide and an alcohol, $R\cdot CO_3H \longrightarrow R\cdot OH + CO_2$, or carbon dioxide and an unsaturated hydrocarbon, $C_nH_{2n+1}\cdot CO_3H = C_nH_{2n} + CO_2 + H_2O$.

By the electrolysis of sulphonediacetic acid or its salts, the products are carbon dioxide and sulphuric acid, and not the expected product, diethylene disulphone. J. F. S.

Determination of the Normal Density of Ethylene. T. BATUECAS (*Anal. Fis. Quim.*, 1918, **16**, 258—281; *Helvetica Chim. Acta*, 1918, **1**, 136—141).—The mean of twenty-one determinations with samples of ethylene prepared from ethyl alcohol by phosphoric acid, boric acid, sulphuric acid, and alumina gave for the normal density the value $L_0 = 1{\cdot}26031$ grams. A. J. W.

Silver Acetylide. JOHN EGGERT (*Zeitsch. Elektrochem.*, 1918, **24**, 150—154. Compare A., 1918, ii, 228).—The amount of gaseous product produced by the detonation of silver acetylide depends on the method of preparation. Silver acetylide prepared

from an acid silver nitrate solution evolves about ten times the volume of gas, on detonation, as does material prepared in ammoniacal solution, neutral solution, or in solution of hydrofluoric acid. The material prepared in nitric acid solution contains 78·5% of silver, and the gaseous product of detonation consists of a mixture of carbon monoxide, carbon dioxide, methane, hydrogen, nitrogen, nitric oxide, and water vapour. The material prepared in 2% ammoniacal solution contains 89·5% of silver, and the product of detonation consists of carbon monoxide, carbon dioxide, methane, hydrogen, and water vapour. The analyses show that the product from nitric acid consists of 57% of silver acetylide and 43% of silver nitrate, whilst that from ammonia consists of 86% of silver acetylide and 14% of silver hydroxide. J. F. S.

Methods of Formation of Chlorohydrins. I. Glyceryl Chlorohydrins. L. SMITH (*Zeitsch. physikal. Chem.*, 1918, **92**, 717—740).—The author has found that the velocity constants for the hydrolysis of chlorohydrins steadily decrease as the action proceeds and has attributed this action to the presence of two (or more) isomerides in the material employed. The nature of the chlorohydrin prepared by the various methods is not well investigated, and the usual methods are not very suitable for recognising these compounds in mixtures. The rate of hydrolysis by alkali hydroxides can be used for this purpose, and from the rate with which the velocity constant changes it is possible to state which isomerides are present. Using this method, the products obtained by the various methods for the preparation of glyceryl chlorohydrin have been examined. (1) Glyceryl monochlorohydrin, prepared from *epi*chlorohydrin, consists entirely of α-monochlorohydrin. (2) Monochlorohydrin from glycerol by the action of hydrogen chloride is a mixture of the α- and β-compounds containing a large excess of the α-derivative. (3) By the action of hypochlorous acid on allyl alcohol, a mixture of the α- and β-chlorohydrins is produced which consists mainly of the β-compound. (4) The monochlorohydrin produced by the action of hydrogen chloride consists of a mixture of 85—90% of the α-compound and 10—15% of the β-compound. A number of experiments are described which are designed to separate the constituents of the mixtures. (5) Glyceryl dichlorohydrin, prepared by the action of chlorine on allyl alcohol, contains only traces of the αγ-compound. (6) The product of the action of hydrogen chloride on *epi*chlorohydrin contains nothing but the pure αγ-compound. (7) The product of the action of hypochlorite on allyl alcohol contains about one-third of its weight of αγ-dichlorohydrin. The whole of the hydrolytic experiments were carried out with both baryta and sodium hydroxide.

J. F. S.

Methods of Formation of Chlorohydrins. II. Propylene Chlorohydrins. LENNART SMITH (*Zeitsch. physikal. Chem.*, 1918, **93**, 59—88. See preceding abstract).—The author has prepared the propylene chlorohydrins by various methods, and has examined

the products by the kinetic method (*loc. cit.*) with the object of ascertaining their composition, and so deciding the best methods for preparing the different isomerides. (1) The product of the action of water on allyl chloride gives pure propylene α-chlorohydrin; (2) by the action of sulphur chloride on propylene glycol, a product containing 25% of the β-compound and 75% of the α-compound is obtained; (3) propylene glycol treated with hydrogen chloride yields more β-chlorohydrin than in case (2); (4) propylene oxide treated with hydrogen chloride yields mainly the α-compound with not inconsiderable quantities of the β-compound; (5) the action of hypochlorite on propylene yields a mixture of the products. Henry's method (A., 1903, i, 725) for converting the α-chlorohydrin into β-chlorohydrin has been examined, and it is shown that the product consists mainly of the α-derivative.

J. F. S.

Autoxidation of some Derivatives of Thioncarbonic Acid. O. BILLETER and B. WAVRE (*Helvetica Chim. Acta*, 1918, 1, 167—174).—Compounds containing the group C:S, and particularly those of the types CS(OR)(SR), $CS(OR)_2$, CSCl(OR), and thiocarbonyl chloride, $CSCl_2$, are phosphorescent and rapidly absorb oxygen, being thereby oxidised. These substances also emit a phosphorescent vapour. The oxidation occurs only in the presence of a catalyst such as a hydroxide of the alkali or alkaline earth metals, alkali carbonates, oxides of zinc or magnesium, and ammonia. Ethyl xanthate in the presence of excess of *N*/10-ammonia solution rapidly absorbs oxygen, and about 90% of the sulphur present is converted into sulphuric acid; some of the compound, OEt·CO·SEt, is also produced. Methyl methylxanthate in the presence of *N*-ammonia is oxidised very rapidly, the sulphur being oxidised to thiosulphate, sulphite, trithionate, and sulphate, whilst hexamethylenetetramine is also formed. Methyl thioncarbonate, $CS(OMe)_2$, is rapidly oxidised, 38% of the sulphur being regained as sulphuric acid, whilst the rest appears as thiosulphuric acid, sulphurous acid, and a little trithionic acid. The ethyl ester, $CS(OEt)_2$, does not undergo autoxidation in the presence of pure oxygen, but with air 40% of the ester is oxidised and 14% of the sulphur appears as sulphuric acid, whilst the rest is obtained as thiosulphuric acid, sulphurous acid and a trace of trithionic acid. The chloro-ester, CSCl·OMe, is oxidised so rapidly that in the first half minute 83% of the theoretical quantity of oxygen is absorbed, 16·9% of the sulphur is oxidised to sulphuric acid, and the residue to sulphurous acid. Thiocarbonyl chloride is very rapidly attacked, but only about 30% is oxidised normally, the residue being absorbed by the ammonia to form ammonium thiocyanate and sulphur.

J. F. S.

Some Metallic Salts and Complex Metallic Derivatives of the Cyanocarboxylic Acids and their Esters. II. LIZZIE PETTERSON-BJÖRCK (*J. pr. Chem.*, 1918, [ii], **97**, 51—58).—An

extension of the earlier paper (A., 1913, i, 27) giving a description of the cobalt and silver salts of cyanoacetic acid and of the platinum derivatives of methyl and ethyl cyanoacetate.

Cobalt cyanoacetate, $(CN{\cdot}CH_2{\cdot}CO_2)_2Co,H_2O$, obtained by the action of cyanoacetic acid on an aqueous suspension of cobalt hydroxide, forms pale red needles, the red aqueous solution of which becomes blue on warming. Silver cyanoacetate, prepared by precipitation from potassium cyanoacetate and silver nitrate in aqueous solution, forms colourless needles (compare Meves, *Annalen*, 1867, **143**, 304). By the interaction of barium cyanoacetate and chrome alum, it is possible to obtain green, prismatic crystals of a chromium cyanoacetate analogous to the ferric salt described earlier (*loc. cit.*). When agitated with an aqueous solution of potassium platinochloride, the methyl and ethyl esters of cyanoacetic acid undergo conversion into the compounds $Pt(CO_2Me{\cdot}CH_2{\cdot}CN)Cl_2$ and $Pt(CO_2Et{\cdot}CH_2{\cdot}CN)Cl_2$ respectively, each crystallising in needles. In the course of attempts to obtain platinum derivatives of free cyanoacetic acid, ammonia platinum sulphate, $Pt(NH_3)_2SO_4$, was treated with dilute aqueous cyanoacetic acid, a blackish-violet, crystalline compound being obtained of the composition $(NH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2)_2Pt$. D. F. T.

Transformation of Methyl α-Elæostearate into Methyl β-Elæostearate. R. S. MORRELL (*J. Soc. Chem. Ind.*, 1918, **37**, 181—182T).—A continuation of the investigation of the properties of thickened drying oils (T., 1918, **113**, 111). The thickened "tung oil" was divided into fractions soluble and insoluble in acetone. The former was converted into the methyl ester by means of sodium methoxide, and this ester on hydrolysis yielded *β-elæostearic acid*; the same result was obtained from the fraction insoluble in acetone. The cerium salt was prepared from the undistilled ester, and since it was completely soluble in ether, it was evidently the salt of the α-acid. The author concludes, therefore, that the stereoisomeric change occurs during the distillation of the ester. J. F. S.

The Ethyl Hydrogen Citrates. L. WOLFRUM and JOH. PINNOW (*J. pr. Chem.*, 1918, [ii], **97**, 23—50. See also A., 1915, ii, 679). —When esterified with ethyl alcohol in the absence of a catalyst, citric acid yields a mixture of *s*- and *as*-ethyl dihydrogen and diethyl hydrogen citrates, of which the constitutions can be distinguished by colorimetric comparison of their ionisation constants (compare Palomaa, A., 1912, i, 6). The α-hydroxy-acids predominate in the product, which also contains a small quantity of derivatives of aconitic acid. It is desirable to exclude moisture as completely as possible during the esterification. The constituent esters of the esterification product can be roughly separated by fractional extraction with ether in a Partheil-Rose apparatus, the final purification of the individual hydrogen esters being effected by recrystallisation of a suitable salt, the calcium salt of the

as-ethyl dihydrogen ester, the zinc salt of the *s*-ethyl dihydrogen ester, and the sodium salt of the *s*-diethyl hydrogen ester being selected for this purpose. As the *as*-diethyl hydrogen citrate is more soluble than its isomeride and has little tendency to the formation of crystalline salts, it is necessary to prepare this by an independent method from ethyl citrate; the partial alkaline hydrolysis of ethyl citrate yields only *as*-diethyl hydrogen citrate, and the further partial hydrolysis of this (or of ethyl citrate) yields *s*-ethyl dihydrogen citrate, so that a convenient method of preparation for each of these two esters is thus supplied (compare Pinnow, this vol., ii, 103; also Meyer, A., 1909, ii, 391, 803). The ester formed during the fermentation of citric acid is a mixture of the ethyl dihydrogen citrates.

s-Diethyl hydrogen citrate, needles, m. p. 58—59°, dissociation *constant* 1·514 *at* 15°, *forms double molecules in ethereal solution*; sodium salt, needles, m. p. 144—145°; *silver* salt, needles; *brucine* salt. The partition coefficient of this ester between ether and water was measured. The *as*-diethyl hydrogen citrate resembles the symmetrical isomeride in possessing a bitter taste, but with the exception of the silver salt, needles, m. p. 109·5—110·5°, the salts are amorphous.

s-Ethyl dihydrogen citrate, for which the partition coefficient between ether and water was determined, forms prisms, m. p. 97·5—98·5°; *silver* salt, tablets; basic *lead* salts,

$$2C_8H_{10}O_7Pb,3C_8H_{10}O_7(PbOH)_2$$

and $3C_8H_{10}O_7Pb,C_8H_{10}O_7(PbOH)_2$; *copper* salt,

$$(C_8H_{10}O_7CuOH)_2Cu,5H_2O,$$

greenish-blue prisms. *as*-Ethyl dihydrogen citrate gave a microcrystalline, basic copper salt, $(C_8H_{10}O_7CuOH)_2Cu,2H_2O$, and a zinc salt, $2C_8H_{10}O_7Zn,(C_8H_{10}O_7ZnOH)_2Zn,13H_2O$; its brucine salt could not be resolved into enantiomorphous forms.

Ethyl citrate is generally contaminated by the presence of ethyl aconitate.

The earlier literature with respect to the ethyl hydrogen citrates is largely misleading and untrustworthy. D. F. T.

Bromination in the α-Position of the Aldehydes of the Fatty Series. ANTONIO MADINAVEITIA and JOSÉ PUYAL (*Anal. Fis. Quim.*, 1918, **16**, 329—337).—The chloro-ethers formed by the action of hydrogen chloride on mixtures of aldehydes and alcohols in equimolecular proportions are converted by bromine at 0° into chlorobromo-ethers, the bromine atom being adjacent to the chlorine. These derivatives are transformed by water into the α-bromoaldehydes, and by alcohols into the corresponding bromoacetals. The following compounds have been prepared: α-chloro-β-bromodiethyl ether, b. p. 64—65°/13 mm.; α-bromoacetal, b. p. 70—72°/20 mm.; methyl α-chloro-β-bromoethyl ether, b. p. 167° (decomp.); *ethyl α-chloro-β-bromoisoamyl ether*, b. p. 94—96°/15 mm.; *α-bromoisovaleraldehyde*, b. p. 55—56°/25 mm.; and the corresponding *diethyl acetal* derivative, $CHMe_2 \cdot CHBr \cdot CH(OEt)_2$, b. p. 105—107°/30 mm. A. J. W.

A New Form of Methylgalactoside and its Conversion into Octamethyldigalactose and into a Methyldigalactoside. MARY CUNNINGHAM (T., 1918, **113**, 596—604).—The isolation of four galactose penta-acetates (Hudson, A., 1916, i, 546) indicates the possible existence of a modification of galactose analogous to γ-dextrose, and it is now shown that the syrupy form of methylgalactoside obtained from methyl alcohol and galactose at 100° in the presence of a little hydrogen chloride (Irvine and Cameron, T., 1905, **86**, 907) is an ether of the γ-series. On methylation by the silver oxide method, the *γ-methylgalactoside* ($[\alpha]_D$ +12·95° in alcohol, +25·9° in water) is converted into tetramethyl γ-methylgalactoside identical with that described previously (Irvine and Cameron, *loc. cit.*), which on hydrolysis yields tetramethyl galactose; this substance at the ordinary temperature undergoes spontaneous polymerisation to *octamethyl γ-digalactose*, $C_{20}H_{38}O_{11}$. On heating methylgalactoside with acidic methyl alcohol, there is obtained an amorphous methyldigalactoside ($[\alpha]_D$ in methyl alcohol, +85·6°; in water, +101·1°) identical with the substance regarded by Fischer (*A.*, *1895*, *i*, *439*) as a methylgalactoside; the result is the same whether the original methylgalactoside is the α-, β-, or γ-form, and it appears probable that in the presence of acidic methyl alcohol any one of these substances gives rise to an equilibrium mixture of all three, the unstable γ-modification then undergoiug hydrolysis to give the reactive type of sugar; the product therefore consists of the stable forms of methylgalactoside (α- and β-) united with the unstable γ-form, the constitution being

$$OMe{\cdot}CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CH{\cdot}CH{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH$$

O (ring, C-1 to C-4) ; O (ring, bridging the two CH groups) .

For experimental details, the original should be consulted.

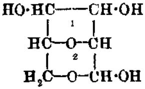
D. F. T.

Application of the Auto-condensation Powers of γ-Sugars to the Synthesis of Carbohydrate Complexes. MARY CUNNINGHAM (T., 1918, **113**, 604—607. Compare preceding abstract).—From the observation that any one of the three methylgalactosides when heated with acidic methyl alcohol gives rise to a mixture of stereoisomeric condensation compounds consisting of the stable α- and β-hexosides united with γ-galactose (preceding abstract), it is possible that similar compounds might be formed by merely dissolving a reducing sugar in this reagent and concentrating the solution. Experiment shows the correctness of this argument, but as the γ-sugar transiently produced may condense with preformed complexes, the products are often of greater complexity than methyldigalactoside (*loc. cit.*). Galactose and dextrose yield respectively a methyltetragalactoside and a methyltetraglucoside, $C_{25}H_{44}O_{21}$, whilst maltose gave a methyltrimaltoside, $C_{37}H_{64}O_{31},H_2O$. Towards Fehling's solution, the products behave as glucosides, whilst they also show the characteristic reactions of γ-compounds.

For experimental details, reference should be made to the original. D. F. T.

The Degradation of Starch by Formaldehyde. H. Maggi and G. Woker (*Ber.*, 1918, **51**, 790—793. Compare A., 1917, i, 447, 686).—It has been shown that the dialysate obtained from a mixture of starch and formaldehyde has the properties of a solution of dextrin and simpler carbohydrates. A precipitate produced by adding alcohol to such a dialysate, redissolved in water, and allowed to become mouldy during the summer vacation, developed dextrose, identified as its osazone. Since the same mould produced dextrose from genuine dextrin, it is obvious that dextrin was present in the original dialysate, and since formic acid has no action on starch under the same conditions, the hydrolysis must be ascribed to the formaldehyde. J. C. W.

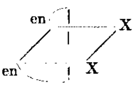
Cellulose and Starch. Jean Sarasin (*Arch. Sci. phys. nat.*, 1918, [iv], **46**, 5—32).—An inquiry into the constitution of cellulose and starch. A careful examination of the products of decomposition by heat of cellulose and starch indicates that in both cases *l*-glucosan is an intermediate product in the breaking-down process, and that this material itself when distilled under reduced pressure gives the same products as do starch and cellulose, in addition to the *l*-glucosan which they yield. Starch and cellulose are thus polymerides of *l*-glucosan, to which the author assigns the constitution (annexed formula), and he considers that it is the ring 2 which opens, giving two free valencies for the polymerisation, since amongst the products of decomposition of starch and cellulose 2:5-dimethylfuran is found. W. G.



Lignin. I. Lignosulphonic Acids. M. Hönig and Jacques Spitzer (*Monatsh.*, 1918, **39**, 1—14. Compare Klason, A., 1908, i, 717).—The lignosulphonic acid obtained from different sulphite liquors varies considerably in composition (compare Seidel, *Mitt. k.k. Tech. Gewerbemuseums Wien.*, 1897, **7**, 287) and consists of a mixture of substances. By fractional precipitation of the calcium or barium salts from aqueous solution by alcohol, it is possible to obtain fractions of distinct composition approximating, for the barium salts, to the formulæ $C_{43}H_{50}O_{18}S_2Ba$, $C_{40}H_{44}O_{18}S_2Ba$, and $C_{74}H_{114}O_{48}S_2Ba$. D. F. T.

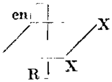
A New Kind of Isomerism with Cobalt Compounds. Compounds containing Asymmetric Cobalt and Carbon. A. Werner (*Helvetica Chim. Acta*, 1918, **1**, 5—32).—Among the three types of optically active cobaltammines which have been pre-

pared by Werner and his co-workers is the type represented by the *cis*-compound, $[XCo\,en_2]X$. If, now, one of the ethylenediamine groups is replaced by an unsymmetrical group, as, for example,

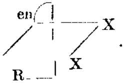


$H_2N{\cdot}CH_2{\cdot}CHR{\cdot}NH_2$,

in place of the configuration (annexed formula), two structural formulæ can be written, since the unsymmetrical molecule can take up two different positions, namely,



and



In the first formula the radicle R is far removed from the plane in which the two X-groups lie, whereas in the second formula it lies close to that plane. It follows that the *cis*-compound $\left[X_2Co\begin{matrix}en\\ A\\ B\end{matrix}\right]X$, where *AB* represents an unsymmetrical group, should give two series of salts. If, for example, *AB* is propylenediamine (pn), there should be two series of *flavo*-salts, and this has actually been found to be the case. The two series are called the α- and β-series, the former giving salts which crystallise in prisms and the latter salts which crystallise in needles.

If, now, optically active propylenediamine is used, as well as optically active cobalt salt, further possibilities of the formation of isomerides occur. These possibilities, all of which have been realised experimentally, may be summarised as follows.

Eight optically active *flavo*-salts are possible, namely,

α- or prismatic series	*d*-propylenediamine	*d*-cobalt
		l-cobalt
	l-propylenediamine	*d*-cobalt
		l-cobalt
β- or needle series	*d*-propylenediamine	*d*-cobalt
		l-cobalt
	l-propylenediamine	*d*-cobalt
		l-cobalt

These optically active compounds can combine in different ways to give partly racemic compounds, which have also been prepared, namely:

(1) Four compounds which are racemic with respect to cobalt.

α- or prismatic series	*d*-pn-*d*-Co + *d*-pn-*l*-Co
	l-pn-*d*-Co + *l*-pn-*l*-Co
β- or needle series	*d*-pn-*d*-Co + *d*-pn-*l*-Co
	l-pn-*d*-Co + *l*-pn-*l*-Co.

(2) Four compounds which are racemic with respect to propylenediamine.

$$\alpha\text{- or prismatic series}\left\{\begin{array}{l} d\text{-Co-}d\text{-pn} + d\text{-Co-}l\text{-pn} \\ l\text{-Co-}d\text{-pn} + l\text{-Co-}l\text{-pn}\end{array}\right.$$

$$\beta\text{- or needle series}\left\{\begin{array}{l} d\text{-Co-}d\text{-pn} + d\text{-Co-}l\text{-pn} \\ l\text{-Co-}d\text{-pn} + l\text{-Co-}l\text{-pn}\end{array}\right.$$

Further, by combination of the α-salts of (1) and (2), and of the β-salts of (1) and (2), two completely racemic, and therefore inactive, compounds can be obtained.

Also, using optically active propylenediamine, the *trans*-isomeride (*croceo*-salt) of the formula $\left[X_2Co^{en}_{pn}\right]X$ *will give rise to three* isomerides, namely:

$$\left.\begin{array}{l} d\text{-}trans\text{-compound} \\ l\text{-}trans\text{-compound}\end{array}\right\} r\text{-}trans\text{-compound.}$$

The compound used as the starting point in this investigation was *dinitroethylenediaminepropylenediaminecobaltic nitrite*,

$$\left[(NO_2)_2Co^{en}_{pn}\right]NO_2.$$

To obtain this, trinitrotriamminecobalt, $(NO_2)_3Co(NH_3)_3$, was prepared by heating Erdmann's salt, $[(NH_3)_2Co(NO_2)_4]K$, with the molecular-equivalent quantity of ammonium nitrate. By the action of ethylenediamine in aqueous solution, the following reaction is made to take place:

$$(NO_2)_3Co(NH_3)_3 + en = \left[(NO_2)_3Co^{NH_3}_{en}\right] + 2NH_3,$$

giving trinitroammine-ethylenediaminecobalt. When this is further treated with the molecular equivalent of active propylenediamine, the following reaction occurs:

$$\left[(NO_2)_3Co^{NH_3}_{en}\right] + pn = \left[(NO_2)_2Co^{en}_{pn}\right]NO_2 + NH_3,$$

both *flavo*- and *croceo*-salts of dinitroethylenediaminepropylenediaminecobaltic nitrite being produced. By adding alcohol to the reaction mixture (in solution), the *flavo*-salts are precipitated, whilst the *croceo*-salts remain in solution and can be obtained by concentration. By heating the crude *flavo*-nitrites with water and sodium bromide the bromides can be obtained, and then transformed into the *d*-bromocamphorsulphonates, which are then resolved and separated by fractional crystallisation. From the pure, active bromocamphorsulphonates the active bromides can be obtained by treatment with hydrobromic acid. The fractional crystallisations involved are long and tedious, and for details the original paper must be consulted.

Resolution of the *flavo*-*d*-pn-salts gave rise to four pure *bromocamphorsulphonates*, which may be called *A*, *B*, *C*, and *D*. The

salts *A* and *B* belong to the prismatic series, and are optical antipodes with respect to cobalt, as was shown by a study of their bromides. They have respectively $[\alpha]_D +10°$, $[\alpha]_E +100°$, and $[\alpha]_D +60°$, $[\alpha]_E +30°$. The salts *C* and *D* belong to the needle series, and are also optical antipodes with respect to cobalt; their specific rotations are respectively $[\alpha]_D +20°$, $[\alpha]_E +120°$ and $[\alpha]_D +0°$, $[\alpha]_E +140°$.

Similarly, resolution of the *flavo-l*-pn-salts gave four pure *bromocamphorsulphonates*, *A*, *B*, *C*, and *D*. The prismatic salts *A* and *B* had $[\alpha]_D +106°$, $[\alpha]_E +10°$, and $[\alpha]_D +62°$, $[\alpha]_E +80°$ respectively. The needle salts *C* and *D* had $[\alpha]_D +70°$, $[\alpha]_E +92°$, and $[\alpha]_D +130°$, $[\alpha]_E +14°$ respectively. The pairs *A* and *B* and *C* and *D* were again optical antipodes with respect to cobalt.

The flavo-*dinitroethylenediaminepropylenediaminecobaltic bromides*, XBr, where $X = \left[(NO_2)_2Co{}^{en}_{pn} \right]$, prepared from the above bromocamphorsulphonates, were all yellowish-brown in colour, *A* and *B* crystallising in prisms and *C* and *D* in needles. The specific rotations, $[\alpha]_D$, for the *d* pn-series were:

	d-Co.	*l*-Co.
Prisms	−30° (*B*)	−60° (*A*)
Needles	−6° (*C*)	−108° (*D*)

The corresponding specific rotations for the *l*-pn-series were:

	l-Co.	*d*-Co.
Prisms	+30° (*B*)	+60° (*A*)
Needles	+6° (*C*)	+108° (*D*)

The flavo-*thiocyanates*, XCNS, were prepared from the bromides by treatment with sodium thiocyanate, and are yellow in colour. The specific rotations, $[\alpha]_D$, of the *d*-pn-series were: *A*, −64°, *B*, −32°, *C*, −6·5°, *D*, −109°, and of the *l*-pn-series: *A*, +64°, *B*, +32°, *C*, +6·5°, *D*, +109°.

The flavo-*sulphates*, X_2SO_4 (the isomeride *A* crystallises with $1H_2O$), were obtained from the bromides by reaction with ammonium sulphate. The specific rotations, $[\alpha]_D$, of the *d*-pn-series were: *A*, −63°, *B*, −32°, *C*, −7°, *D*, −112°, and of the *l*-pn-series, *A*, +63°, *B*, +32°, *C*, +7°, *D*, +112°.

The *partly racemic* flavo-*bromides*, XBr, were prepared synthetically by combining the proper constituents in pairs. The following compounds containing racemic cobalt and active propylenediamine were obtained. d-*pn-Series*: *A*+*B*, $[\alpha]_D -45°$; *C*+*D*, $[\alpha]_D -57°$. l-*pn-Series*: *A*+*B*, $[\alpha]_D +45°$; *C*+*D*, $[\alpha]_D +57°$. The compounds containing racemic propylenediamine and active cobalt were as follows: *d*-pn-*A*+*l*-pn-*B*, $[\alpha]_D -15°$; *d*-pn-*B*+*l*-pn-*A*, $[\alpha]_D +15°$; *d*-pn-*C*+*l*-pn-*D*, $[\alpha]_D +51°$; *d*-pn-*D*+*l*-pn-*C*, $[\alpha]_D -51°$.

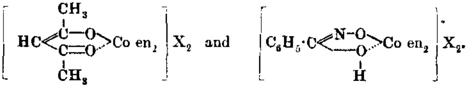
All the above *flavo*-salts show strong optical dispersion, and curves are given showing their rotations for fifteen wave-lengths between $\mu\mu = 643·25$ and 492.

The completely *racemic* flavo-*salts* were prepared synthetically from the proper components, and were found to be inactive.

The croceo-*chlorides*, XCl, were prepared from the crude nitrites by treatment with cooled hydrochloric acid. They are golden-yellow in colour and less soluble than the bromides and iodides. The *d*-pn-chloride has $[\alpha]_D -11°$ and the *l*-pn-chloride $[\alpha]_D +12°$.

The d-*pn*- and l-*pn*-croceo-*nitrites*, XNO_2, have $[\alpha]_D \mp 22°$, and the corresponding croceo-*bromides* $[\alpha]_D \mp 10°$. T. S. P.

Constitution of Internally Complex Metallic Salts. A. Werner and Soph. Matissen (*Helvetica Chim. Acta*, 1918, 1, 78—84).—Tschugaev has already shown that when dioximes are introduced into metal-ammonias, the dioximino-radicle occupies two co-ordination positions. In order to see if this holds in other cases, the authors have introduced acetylacetone and benzhydroxamic acid, which readily give internally complex salts, into cobalt-ammonias, and have found that these also occupy two co-ordination positions. The action of acetylacetone and benzhydroxamic acid respectively on hydroxoaquodiethylenediaminecobalt salts gives rise to acetylacetonato- and benzhydroxamato-diethylenediaminecobalt salts, which have the following general formulæ:



Acetylacetonatodiethylenediaminecobalt bromide, YBr_2,H_2O, where $Y=[C_5H_7O_2Co\,en_2]$, is prepared by heating a solution of 1 gram of hydroxoaquodiethylenediaminecobalt bromide in 10 c.c. of water with 0·6 gram of acetylacetone on the water-bath under reflux for half an hour, and then concentrating to half its volume. The bromide is precipitated by the addition of sodium or potassium bromide, and forms large, garnet-red crystals. By appropriate double decomposition of the bromide with other salts, as, for example, with potassium iodide to give the iodide, or with silver chloride to give the chloride, the following salts were prepared. The *iodide*, YI_2,H_2O, forms garnet-red prisms; the *chloride*, $YCl_2,2H_2O$, gives dark red crystals; the *nitrate*, $Y(NO_3)_2$, crystallises in large, well-developed garnet-red crystals; the *sulphate*, $YSO_4,2H_2O$, forms long, red needles; and the *perchlorate*, $Y(ClO_4)_2$, crystallises in large, ruby-red columns.

Benzhydroxamatodiethylenediaminecobalt bromide, YBr_2, where $Y=[C_7H_6O_2NCo\,en_2]$, is prepared by heating a solution of 1 gram of hydroxoaquodiethylenediaminecobalt bromide in 10 c.c. of water with the molecular-equivalent quantity of benzhydroxamic acid under reflux for half an hour. The solution is filtered from a light-coloured by-product and the bromide precipitated by the addition of sodium or potassium bromide. It forms large, almost black crystals with a metallic glance. The following salts were prepared from the bromide by methods similar to those mentioned for the acetylacetonato-salts. The *perchlorate*, $Y(ClO_4)_2$, forms large,

violet crystals possessing a metallic glance; the *dithionate*, $YS_2O_6,2H_2O$, crystallises in fine needles; the *thiocyanate*, $Y(SCN)_2$, gives dark violet, metallic-glistening octahedra; and the *sulphate*, $YSO_4,3H_2O$, crystallises in rose-coloured, long, hair-like needles.

T. S. P.

The Constitution of Carbamides. VI. Mechanism of the Synthesis of Urea from Urethane. EMIL ALPHONSE WERNER (T., 1918, **113**, 622—627).—Although the vapour density of urethane at 203° approximates to the theoretical, the ester gradually decomposes when boiled under reflux, yielding ethyl alcohol and cyanic acid, the latter being found as cyanuric acid. The formation of urea from ammonia and urethane is therefore not a simple case of the conversion of an ester into an amide, but is actually a modification of Wöhler's synthesis, involving the union of ammonia and cyanic acid. Similarly, the decomposition of urethane by aqueous alkali is not a direct hydrolysis, as is commonly assumed, but actually occurs by the stages $OEt{\cdot}CO{\cdot}NH_2 \longrightarrow OEt{\cdot}C(ONa){:}NH \longrightarrow EtOH + NaOCN \longrightarrow NaHCO_3 + NH_3$. On the other hand, when heated in a current of hydrogen chloride, urethane gives carbon dioxide, ethyl chloride, and alcohol, the acid therefore appearing to favour the constitution $OEt{\cdot}CO{\cdot}NH_2$, whereas alkali favours the constitution $OEt{\cdot}C(OH){:}NH$. When urethane is heated in aqueous solution at 130°, it gives rise to urea without the independent addition of ammonia, the cyanic acid arising from the dissociation of the urethane undergoing hydrolysis to urea. The relative difficulty of formation of urea from ethyl carbonate or carbamate and ammonia supports the view that urea does not contain two amino-groups, and the suggestion is made that two amino-groups, like two hydroxyl groups, cannot be attached stably to one carbon atom.

For experimental details, reference should be made to the original.

D. F. T.

The Constitution of Dicyanodiamide. WILLIAM J. HALE and FRANK C. VIBRANS (*J. Amer. Chem. Soc.*, 1918, **40**, 1046—1063).—Of the many constitutions which have been proposed for dicyanodiamide, the authors' experiments favour the cyanoguanidine structure, $NH_2{\cdot}C({:}NH){\cdot}NH{\cdot}CN$, suggested by Bamberger in 1880. Pohl (A., 1908, i, 575) found that about one-half of the total nitrogen in the molecule is eliminated by sodium hypobromite, and, assuming that only an amino-group can react to this end, proposed the constitution $C(NH_2)_2{:}N{\cdot}CN$. The authors, however, using 20% sodium hypochlorite, have eliminated three-fourths of the nitrogen, the remaining atom being that in the cyano-group.

The quantity of nitrogen liberated by the reaction between dicyanodiamide and nitrous acid depends on the temperature and the concentration of the acid used as solvent. With 50% acetic acid as solvent, no nitrogen was evolved at the ordinary temperature, and at the b. p. only an amount corresponding with one-

quarter of an atom. With 85% acetic acid at the b. p. one atom of nitrogen was eliminated, with 95% acid two atoms, with glacial acetic acid about three atoms, whilst with 85% phosphoric acid all the nitrogen in dicyanodiamide was eliminated in the elementary state. Dicyanodiamide, therefore, undoubtedly contains one amino-group, as is evidenced by the comparative ease with which the first atomic proportion of nitrogen is eliminated. If a second amino-group were present, its interaction with nitrous acid should proceed under practically the same conditions. The development of a second amino-group in the course of the decomposition might therefore account for the higher temperature and longer time necessary for interaction with a second molecule of nitrous acid. The authors have failed to find a compound containing an amino-group which in 85% acetic acid at the b. p. does not react with nitrous acid; even guanidine, which, as stated by Van Slyke, fails to yield any nitrogen in 50% acetic acid at the ordinary temperature, yields two atomic proportions (but never more than two) in hot, more concentrated acetic acids. The fact that the condensation product of dicyanodiamide and formaldehyde, to which Pohl (*loc. cit.*) ascribes the constitution $OH\cdot CH_2\cdot NH\cdot C(NH_2)\colon N\cdot CN$ derived from his formula for dicyanodiamide, does not yield any nitrogen in 85% acetic acid suffices, therefore, to disprove Pohl's constitution, leaving for the condensation product the alternative constitution $OH\cdot CH_2\cdot NH\cdot C(\colon NH)\cdot NH\cdot CN$ derived from the Bamberger formula for dicyanodiamide.

When an aqueous solution of dicyanodiamide and acetylacetone is boiled with a little 2*N*-sodium hydroxide, a substance, $C_7H_8N_4$, is obtained which does not contain a primary amino-group, but responds to the Liebermann and the Hinsberg tests for secondary amines. The formation of this substance disproves, according to the authors, Pohl's formula for dicyanodiamide, since they assert that this would lead to the formula of a condensation product containing neither primary nor secondary amino-groups. The substance $C_7H_8N_4$ is regarded as *2-imino-1-cyano-4:6-dimethyl-1:2-dihydropyrimidine*, $NH\colon C<\begin{matrix}N\!=\!=\!=\!CMe\\ N(CN)\cdot CMe\end{matrix}>CH$. It forms colourless needles, m. p. 225°, yields a *silver* salt, $C_7H_7N_4Ag$, and is converted by boiling dilute sulphuric acid (1:5) into *2-imino-4:6-dimethyl-1:2-dihydropyrimidine*, $C_6H_9N_3,H_2O$, lemon-yellow prisms, m. p. 199° (decomp.; anhydrous), which yields the well-known acetylacetonecarbamide when boiled with 4*N*-sodium hydroxide.

The condensation of dicyanodiamide (Bamberger's formula) and acetylacetone could yield a product which might be 2-imino-1-cyano-4:6-dimethyl-1:2-dihydropyrimidine (as stated above) or 2-cyanoamino-4:6-dimethylpyrimidine, but the latter alternative is excluded, because the product does not give Combes's aminodimethylpyrimidine on hydrolysis with boiling dilute sulphuric acid.

C. S.

Mercury Fulminate. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1918, **37**, 190T).—The author points out that mercury fulminate

cannot be formed in the absence of nitrous acid or a mixture of nitric oxide and nitrogen peroxide; he therefore represents the formation and constitution of fulminic acid by the equation:

$$\begin{array}{l}CH_3\\ |\\ OH{\cdot}CH_2\end{array} + \begin{array}{l}O{:}N\\ O{:}N\end{array}\!\!>O = \begin{array}{l}CH{:}N\\ |\\ OH{\cdot}C{=\!=}N\end{array}\!\!>O + 2H_2O.$$

J. F. S.

The Decomposition of Solutions of Hydrocyanic Acid. W. LEWCOCK (*Pharm. J.*, 1918, **101**, 50—51).—The decomposition of solutions of hydrocyanic acid with the formation of a yellow or brown coloration or deposit is attributed to the action of small quantities of basic substances which are principally derived from the glass vessels, but might also be introduced by the use of hard water in preparing the solutions. A similar decomposition is observed in concentrated solutions of sodium cyanide on the addition of sodium carbonate, but not in presence of sodium hydroxide. In this case, it would appear that the alkali influences the hydrogen cyanide liberated by hydrolysis of the cyanide, whereas in presence of sodium hydroxide this hydrolysis is suppressed. Experiments showed that the addition of bases and salts with alkaline reaction greatly accelerated the decomposition of dilute solutions of hydrocyanic acid. The effect of bases derived from glass was studied by sealing up portions of an 8% solution of hydrocyanic acid with finely powdered glass, together with various substances which might be expected to retard the decomposition, and observing the length of time required for the appearance of a yellow coloration. The retardation was most marked in the presence of acids, and the addition of 1% of sulphuric acid, calculated on the weight of hydrocyanic acid, delayed the appearance of the colour for twenty-three days, as compared with two days in the case of the solution of hydrocyanic acid in distilled water. Tartaric acid equivalent to half the above quantity of sulphuric acid preserved the solution for twelve days, and saturation with carbon dioxide delayed decomposition for thirteen days. The preservative effect of various substances in the presence of glass would therefore appear to depend essentially on their acidity, and it was found that substances such as alcohol, glycerol, and mannitol were entirely without influence. With a higher concentration of tartaric acid (0·04 gram in 5 c.c.), the 8% solution of hydrocyanic acid remained unaffected in the presence of glass for more than four months, and it is concluded that 10% of sulphuric acid, on the weight of the hydrocyanic acid, would preserve the solution indefinitely.

J. F. B.

Complex Uranyl Compounds. ARNO MÜLLER (*Zeitsch. anorg. Chem.*, 1918, **103**, 55—68).—A number of complex compounds of the uranyl radicle with cacodylic acid, *o*-, *m*-, and *p*-sulphaminobenzoic acids, toluene-*o*-sulphonic acid, and α-phenylcinchonic acid have been prepared. The cacodylic acid compound

is of special interest on account of its therapeutic properties. By treatment with hydrogen sulphide in alcoholic suspension, it is converted into a dithio-derivative.

Uranyl cacodylate, $UO_2[AsO_2(CH_3)_2]_2$, is prepared by double decomposition of sodium cacodylate and uranyl acetate. It forms a bright yellow, odourless, and tasteless powder, is decomposed by acids and alkalis, and when strongly heated evolves cacodyl vapours, leaving a residue of U_3O_8.

Uranyl thiocacodylate, $UO_2[AsOS(CH_3)_2]_2$, is difficult to isolate owing to its instability. By evaporating its alcoholic solution in a vacuum desiccator, it is obtained as a reddish-brown, crystalline mass with a mercaptan-like odour, m. p. 60—65°.

Uranyl o-*sulphaminobenzoate*, $UO_2[C_6H_4(SO_2\cdot NH_2)\cdot CO_2]_2,3H_2O$, forms small, greenish-yellow crystals with a metallic taste. *Uranyl* m-*sulphaminobenzoate* forms a dihydrate. *Uranyl* p-*sulphaminobenzoate* forms a monohydrate.

Uranyl toluene-o-*sulphonate*, $UO_2[C_7H_7\cdot SO_3]_2,2H_2O$, forms fairly large, bright yellow leaflets.

Uranyl α-*phenylcinchonate*, $UO_2[C_9NH_5Ph\cdot CO_2]_2$, is a dark yellow, tasteless and odourless amorphous powder. E. H. R.

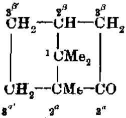
Dissociation as a General Phenomenon with Hydrocarbons. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1918, **39**, 107—128).—The observed action of heat on organic substances, particularly hydrocarbons, indicates the occurrence of dissociation of hydrogen from carbon at a C–H-linking; the effect is not appreciable at the ordinary temperature, but becomes so when the dissociation process is favoured by rise of temperature, the influence of light, and of electrical or radioactive radiation. Substances which will remove one or other of the products of the dissociation should also extend its effect, and examples are quoted in which oxidation is already known to cause a condensation of two aromatic nuclei. The general evidence supplied by the nature of the constituents of coal tar supports the further view that in pyrogenic reactions long side-chains tend to become shortened, and this accords well with the fact that longer chains are more easily attacked, for example, by oxidising agents.

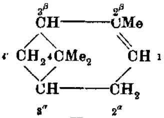
An examination of anthracene oil revealed the presence of diphenyl, together with a mixture of the ditolyls, but dibenzyl could not be detected. *iso*Propylbenzene when heated strongly decomposes mainly into toluene and trioxymethylene, the latter arising from the severed methylene groups. Methyl phthalate gives methyl benzoate, formaldehyde, and methyl diphenyltricarboxylate. Methyl acetate gives α-trioxymethylene as the main product, and no ethyl succinate. The action of sunlight on a suspension of ethyl dihydrolutidinedicarboxylate in benzene gives ethyl lutidinedicarboxylate. D. F. T.

Nomenclature of Singly- and Multiply-divided Carbon Rings. Bridge Linking. J. BREDT and MARIA SAVELSBERG (*J. pr. Chem.*, 1918, [ii], **97**, 1—22).—After reviewing the various

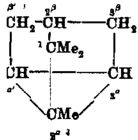
methods of nomenclature suggested hitherto for cyclic organic compounds containing bridged linkings and indicating their respective weaknesses, the authors suggest a scheme in which as far as possible the numbering of the carbon atoms is commenced at an atom possessing no symmetrical counterpart in the molecule, and, in the numbering, careful consideration is given to planes of symmetry in the molecule. The conception of a "bridge" is limited by the exclusion of molecules in which the bridge exists between two ortho-positions in a *cyclo*hexane ring, such compounds, for example, decahydronaphthalene, being classified as containing condensed nuclei. With more complex cyclic molecules, the excesive use of numbers is avoided as far as possible by the use of names, so that each number represents a single position. The various cyclic systems as far as possible are referred to *cyclo*hexane, and are grouped into (*a*) single rings, (*b*) double rings containing a meta- or para-bridge, or composed of rings condensed together by an amphi- or a spiro-attachment, aud polycyclic compounds containing bridges together with a peri-linking, or consisting of combinations of (*a*) and (*b*).

The following examples illustrate this system of nomenclature. In the camphane and fenchane group, the molecule of camphor (annexed formula, I) may be taken as typical, the corresponding name being *p-meso*methylene-1 : 1 : 2^{α}-trimethyl*cyclo*hexan-3^{α}-one. The atoms in compounds of the pinane group are distinguished by

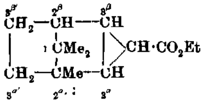

(I.)

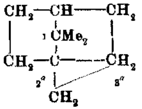

(II.)

the method shown in formula II (annexed), which shows pinene to be *m-meso*methylene-4 : 4 : 2^{β}-trimethyl*cyclo*-$\Delta^{1, 2\beta}$-hexene. By the idea of a bridged ring as defined above, the carane group is excluded from the new system of nomenclature; its inclusion offers no great difficulty, but preference is given to the description of carane as *amphi*methylene*cyclo*hexane. The carbon atoms in tricyclene (*a-pericyclo*camphane) are numbered as in formula III (annexed), the corresponding name being *p-meso*methylene-1 : 1 : 2^{α}-trimethyl-$3^{\alpha\alpha'}$-*pericyclocyclo*hexane, whilst as further examples may be mentioned Buchner's condensation product of ethyl diazoacetate and bornylene, which receives the name ethyl *p-meso*methylene-1 : 1 : 2-trimethyl*cyclo*hexane-*amphi*-$3^{\alpha\beta}$-methylenecarboxylate (formula IV), and the parent hydrocarbon of Forster's hydroxy-


(III.)

camphene (formula V), which is described as *p-meso*methylene-1 : 1-dimethyl*cyclo*hexane-*amphi*-2^a : 3^a-methylene.


(IV.)


(V.)

D. F. T.

Nitrosotriphenylamine and Colours of the Second Order. JEAN PICCARD and MORRIS KHARASCH [and, in part, E. H. FLECK] (*J. Amer. Chem. Soc.*, 1918, **40**, 1074—1079).—It is well known that the colour of a yellow dye is lowered by increase of molecular weight through orange, red, violet, blue, to green owing to a shift of its maximum absorption band towards the red end of the spectrum. Absorption colours have much in common with interference colours, and the first absorption band or group of bands is always followed by a second one, which is the octave of the first. When a dye with a lower colour than green is prepared, therefore, colours of the second order are obtained (Piccard, A., 1913, i, 895), but hitherto dyes giving more than a yellowish-green or greenish-yellow have not been prepared. The authors have now prepared an orange compound of the second order. A suspension of triphenylamine (prepared by heating diphenylamine and iodobenzene in nitrobenzene with an excess of potassium carbonate and a little catalytic copper at 207° for twelve hours) in absolute alcohol saturated with hydrogen chloride was slowly treated at −5° with amyl nitrite, dry hydrogen chloride being passed through the mixture. The crude, orange-red or carmine hydrochloride is suspended in cold water for two hours, the resulting crude base is collected, washed with cold water, dried in a vacuum desiccator, dissolved in dry ether, and the solution treated with hydrogen chloride, whereby p-*nitrosotriphenylamine hydrochloride* (*diphenylbenzoquinonemonoimine oxime chloride*), $OH{\cdot}N{:}C_6H_4{:}NPh_2Cl$, is obtained; it crystallises in long, brown needles, m. p. 178°. p-*Nitrosotriphenylamine* $NO{\cdot}C_6H_4{\cdot}NPh_2$, obtained by hydrolysing the preceding hydrochloride with water, forms long, brown needles (orange when powdered), m. p. 120·5° (corr.), gives a yellow solution in benzene and an orange solution in alcohol, and yields Herz's *p*-acetylaminotriphenylamine by reduction with zinc and acetic acid, followed by acetylation. The colours of the base and its hydrochloride are alike, but that of the former is orange of the second order and that of the hydrochloride orange of the first order. C. S.

Sulphur β-Naphthyl Chlorides. [β-Chlorothiolnaphthalenes.] TH. ZINCKE and K. EISMAYER (*Ber.*, 1918, **51**, 751—767 Compare A., 1912, i, 762; 1915, i, 234).—When β-thiolnaphthalene

is treated with chlorine, it first suffers oxidation to the disulphide, then changes into the unstable β-chlorothiolnaphthalene, and finally yields 1-chloro-β-chlorothiolnaphthalene. This is a comparatively stable substance, capable of taking part in many reactions, a number of which are described.

β-Thiolnaphthalene is obtained by the reduction of crude naphthalene-β-sulphonyl chloride with zinc dust in alcoholic solution. *β-Chlorothiolnaphthalene*, prepared by the action of chlorine (1 mol.) in dry chloroform, is a yellowish-red powder, m. p. 50—60°, which readily changes into di-β-naphthyl disulphide on treatment with alkalis, alcohol, acetone, aniline, or β-naphthol, or when kept. *1-Chloro-β-chlorothiolnaphthalene*, $C_{10}H_6Cl{\cdot}SCl$, the product obtained by using twice the amount of chlorine, forms small, hard, yellowish-red crystals, m. p. 74—75°. This is oxidised by chlorine in glacial acetic acid solution to 1-chloronaphthalene-β-sulphonyl chloride, m. p. 84—85° (compare Cleve, A., 1892, 345), the corresponding *anilide* having m. p. 171—172°.

Methyl 1-chloro-β-naphthylsulphinite, $C_{10}H_6Cl{\cdot}S{\cdot}OMe$, an almost colourless, unstable oil, is prepared by the action of dry sodium methoxide on the chlorothiol, but the corresponding acid is unknown. Attempts to isolate it, for example, by the action of *N*-sodium carbonate on the chlorothiol, result in the formation of the anhydride, *di-1-chloro-β-naphthyl sulphoxide* [*di-1-chloro-β-thionaphthyl oxide*], $O(S{\cdot}C_{10}H_6Cl)_2$, which separates in pale yellow crystals, m. p. 149°. This is reconverted into the chlorothiol by means of phosphorus pentachloride, whilst warm *N*-sodium hydroxide transforms it into *di-1-chloro-β-naphthyl disulphide*, $S_2(C_{10}H_6Cl)_2$, thin, glistening leaflets, m. p. 141—142°, and *1-chloro-β-naphthylsulphinic acid*, $C_{10}H_6Cl{\cdot}SO_2H$, felted needles, m. p. 138—139° (*methyl* ester, from the silver salt, long needles, m. p. 139—140°). If the oxide is boiled with glacial acetic acid, it changes into *di-1-chloro-β-naphthyl disulphoxide*,

$$C_{10}H_6Cl{\cdot}SO{\cdot}SO{\cdot}C_{10}H_6Cl;$$

this may also be prepared by the interaction of the chlorothiol and the silver salt of the foregoing sulphinic acid, and it crystallises in colourless, prismatic needles, m. p. 152—153°, and liberates iodine from potassium iodide.

The chlorothiol reacts with bases in indifferent solvents to form "thiolamines" and "dithiolimines," $C_{10}H_6Cl{\cdot}S{\cdot}NR_2$ and

$$NR(S{\cdot}C_{10}H_6Cl)_2,$$

where R = H or a radicle. Thus, aqueous ammonia yields *1-chloro-β-naphthylthiolamine*, which crystallises in small, stout needles, m. p. 160° (becomes red at 95° and partly decomposes at 105—110°), and forms a *benzylidene* compound, $C_{10}H_6Cl{\cdot}S{\cdot}N{:}CHPh$, m. p. 106—107°. Ethereal ammonia produces *di-1-chloro-β-naphthyldithiolimine* as a pale pink powder, m. p. 213—214°, which may also be obtained by treating the amine with glacial acetic acid in the cold. Methylamine yields *1-chloro-β-naphthylthiolmethylamine*, small leaflets, m. p. 89—90°, and the *imine*, $NMe(S{\cdot}C_{10}H_6Cl)_2$, m. p. 177—178°. *1-Chloro-β-naphthylthiolanilide*, prismatic

needles, m. p. 132°, -*α-naphthylidide*, hard crystals, m. p. 154°, and -*β-naphthylidide*, small needles, m. p. 132—133°, are prepared from the amines in benzene solution.

The naphthylamines behave differently if applied to the chlorothiol in warm glacial acetic acid solution. In these circumstances, the reaction resembles the coupling of a diazonium chloride with the bases. Thus, α-naphthylamine yields 2:4-*di-1′-chloro-β-naphthylthio-α-naphthylamine* [*1-aminonaphthyl 2:4-di-1′-chloro-β-naphthyl disulphide*], $NH_2\cdot C_{10}H_5(S\cdot C_{10}H_6Cl)_2$, m. p. 85—87°, which forms an *acetyl* derivative, m. p. 144—145°, and a red azo-dye with β-naphthol, whilst β-naphthylamine gives 1-*chloro-β-naphthyl 2-amino-α-naphthyl sulphide*, in prisms and needles, m. p. 183—184°. The latter yields a *diacetyl* derivative, m. p. 153—154°, gives azo-dyes, and reacts with the original chlorothiol to form the *compound*, $C_{10}H_6Cl\cdot S\cdot NH\cdot C_{10}H_6\cdot S\cdot C_{10}H_6Cl$, m. p. 187—188°.

The chlorothiol also resembles a diazonium chloride in its reactions with tertiary aromatic amines and phenols, except that the components usually need to be heated to ensure success. Dimethylaniline yields p-*dimethylaminophenyl 1-chloro-β-naphthyl sulphide*, $C_{10}H_6Cl\cdot S\cdot C_6H_4\cdot NMe_2$, prisms and needles, m. p. 120—121°. α-Naphthol gives 1-*chloro-β-naphthyl 4-hydroxy-α-naphthyl sulphide*, $C_{10}H_6Cl\cdot S\cdot C_{10}H_6\cdot OH$, m. p. 116—118° (*acetate*, m. p. 138—139°); β-naphthol forms 1-*chloro-β-naphthyl 2-hydroxy-α-naphthyl sulphide*, large needles, m. p. 142—143° (*acetate*, m. p. 123—124°); and resorcinol yields op-*dihydroxyphenyl 1-chloro-β-naphthyl sulphide*, glistening leaflets, m. p. 153—154° (*diacetate*, m. p. 83—84°).

The chlorothiol also reacts with a number of ketones. For example, acetone gives 1-*chloro-β-naphthyl acetonyl sulphide* (*1-chloro-β-naphthylthiomethyl methyl ketone*),

$$C_{10}H_6Cl\cdot S\cdot CH_2\cdot COMe,$$

in colourless needles, m. p. 70—71°, which forms a *hydrazone*, glistening leaflets, m. p. 202°.

Potassium cyanide converts the chlorothiol into 1-*chloro-β-naphthyl thiocyanate*, $C_{10}H_6Cl\cdot SCN$, m. p. 118—119°.

J. C. W.

Preparation of a New Type of Organic Sulphur Compound. GERALD NOEL WHITE (T., 1918, **113**, 608—609).—When β-naphthyl disulphide is heated with sodium sulphide crystals and sulphur, it gradually dissolves in the sodium polysulphide solution first formed. On cooling, glistening lamellæ of *sodium β-naphthylthiosulphoxylate* separate, from which the free *acid*,

$$\begin{matrix} C_6H_4\cdot CH \\ CH{=}CH \end{matrix}\!\!>\!C\cdot S\cdot SH,$$

is liberated by dilute hydrochloric acid. The *lead* salt, obtained by double decomposition as an orange precipitate, on keeping gradually decomposes, the colour passing through scarlet to brown and black, whilst when heated with alcohol it yields β-naphthyl disulphide.

D. F. T.

The Hydrindene-1 : 2-diols. J. BÖESEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1186—1191).—The authors have repeated the work of Heusler and Schieffer (compare A., 1899, i, 365), and consider that they had obtained an impure *cis*-1 : 2-dihydroxyhydrindene, which is now found to have m. p. 107·5—108°. The diol described by Weissgerber (A., 1911, i, 623) is not really pure, but when obtained in the pure state from indene dibromide it is the *trans*-1 : 2-dihydroxyhydrindene, m. p. 159·8—160° (corr.). It gives a *diacetate*, b. p. 169—169·5°/13 mm. (corr.), $D_4^{20.4}$ 1·1771, n_D^{20} 1·5170. The cis-*dibenzoate* has m. p. 109·5—110·5° (corr.), and the trans-*dibenzoate*, m. p. 76·5—77·5° (corr.), whilst the corresponding *phenylurethanes* have m. p. 205° (decomp.; corr.) and 206·5° (decomp.; corr.) respectively. A polymorphic modification of the *cis*-diol, m. p. 100·5—101·5° (corr.), obtained during the hydrolysis of the *cis*-dibenzoate, is described.

Indene oxide, $\begin{matrix}CH_2-CH\\ | \quad\quad | \\ C_6H_4\cdot CH\end{matrix}\!\!>O$, m. p. 31—31·5°, b. p. 113°/19·5 mm. (corr.), $D_4^{23.6}$ 1·1258, $n_D^{23.1}$ 1·5627, was obtained by the decomposition of bromohydroxyhydrindene by potassium hydroxide in ether. This oxide, as well as the *cis*- and *trans*-dihydroxyhydrindenes, readily gave β-hydrindone when warmed with dilute sulphuric acid. Indene oxide when carefully hydrated gave a mixture of the *cis*- and *trans*-glycols. W. G.

Synthesis of Derivatives of Phenylethyl Alcohol. JOSÉ RANEDO (*Anal. Fis. Quim.*, 1918, **16**, 351—354).—Magnesium benzyl chloride and chloromethyl ethyl ether, $CH_2Cl\cdot OEt$, react to form *phenylethyl ethyl ether*, $CH_2Ph\cdot CH_2\cdot OEt$, a liquid, b. p. 193—196°. Oxidation with chromic acid converts this substance into benzoic acid, and phosphorus pentachloride yields a liquid which decomposes when distilled at ordinary pressure into hydrogen chloride and a liquid, b. p. 200°. A. J. W.

Sitosterol. A. WINDAUS and ERIK RAHLÉN (*Zeitsch. physiol. Chem.*, 1918, **101**, 223—235).—In the presence of palladium, sitosterol in acetic acid solution is reduced by hydrogen at 100°, forming *sitostanol*, $C_{27}H_{48}O$, flat four- or six-sided plates from alcohol, m. p. 137°, $[\alpha]_D^{6}$ +27·9°; *acetate*, m. p. 132°. The new compound closely resembles cholestanol, and on oxidation with chromic acid yields *sitostanone*, $C_{27}H_{46}O$, plates from alcohol, m. p. 157°, $[\alpha]_D^{4}$ +45·7°, and, with excess of chromic acid, *sitostandicarboxylic acid*, $C_{27}H_{46}O_4$, plates from acetic acid, m. p. 225—227°. Both the latter compounds are analogous to, but not identical with, the corresponding cholesterol derivatives, cholestanol, and cholestandicarboxylic acid. On distillation of a mixture of sitostandicarboxylic acid and acetic anhydride at 280° in a vacuum, carbon dioxide and water are evolved, and a cyclic *ketone* produced, $C_{26}H_{44}O$, well-formed hexagonal crystals from methyl alcohol, m. p. 112°. Reduction of sitostanone with zinc amalgam in boiling acetic

acid solution yields the hydrocarbon, *sitostan*, $C_{27}H_{48}$, m. p. 85—85·5°, which resembles cholestan (m. p. 80—81°), but is certainly not identical with it. The observed differences between these derivatives of sitosterol and the corresponding ones derived from cholesterol indicate that the general resemblance of the parent substances cannot be ascribed to the possession of a common structure with a difference in the position of the hydroxyl radicle, the double linking, or of both. The difference between sitosterol and cholesterol must therefore be structural or steric. H. W. B.

Anodic Formation of Ester simultaneously with Nitrobenzene and *o*-Nitrophenol from the Mononitrobenzoic Acids. C. SCHALL (*Zeitsch. Elektrochem.*, 1918, **24**, 154—157).—A mixture of potassium *o*-nitrobenzoate and the free acid in acetic anhydride solution has been subjected to electrolysis at the ordinary temperature. The anode products of the electrolysis were nitrobenzene, *o*-nitrophenol, and the *o*-nitrophenyl ester of *o*-nitrobenzoic acid. The yield of the products depends on the temperature. In concentrated aqueous solutions of potassium acetate and *o*-nitrobenzoate, the anode products are nitrobenzene, *o*-nitrophenol, and methyl *o*-nitrobenzoate. The formation of the nitrophenol is to be regarded as an anodic oxidation product, since this substance is produced by the action of persulphate on the *o*-nitrobenzoate. The formation of nitrobenzene, which is the analogue of methane in the acetate electrolysis, is stated to be due to the thermal decomposition of an intermediate compound of a peroxide nature. J. F. S.

The Direct Conversion of Nitriles into Esters. PAUL PFEIFFER (*Ber.*, 1918, **51**, 805).—With reference to Spiegel's communication (this vol., i, 216), the author points out that examples of the direct conversion of nitriles into esters were given in his work on stilbene-*o*-carboxylic acids some years ago (A., 1911, i, 448), where he also directed attention to the steric hindrance of a methyl group in the ortho-position. J. C. W.

Direct Preparation of Aromatic Nitriles by Catalysis. ALPH. MAILHE (*Bull. Soc. chim.*, 1918, [iv], **23**, 235—238).—Aromatic nitriles may be readily prepared with good yield by passing the vapours of the esters of the corresponding acids along with ammonia over aluminium or thorium oxides at 470—480°. This method has been successfully used with the methyl, ethyl, propyl, or *iso*amyl esters of benzoic, the three toluic, phenylacetic, and α- and β-naphthoic acids. W. G.

The Nature of Subsidiary Valencies. XVIII. Octammines. Influence of the Volume of the Anion. FRITZ EPHRAIM [with E. ROSENBERG] (*Ber.*, 1918, **51**, 644—669. Compare this vol., ii, 115).—In the course of this work it has often been demonstrated that the ability of a substance to form additive compounds is intimately connected with the magnitude of the space

occupied by the various parts of the molecule. It is now shown that when the anion is particularly large, the additive capacity of the cation for negative substances becomes much more than it is normally. For example, very few cases of metallic ammines are known in which the number of molecules of ammonia is more than six, but several are now described, being salts of bivalent metals with aromatic acids, in which the number is eight. In explaining this, the autbor offers a picture of the arrangement of the metallic atoms within the crystal, each one surrounded by eight acid radicles; the larger these radicles are, the more room will there be for ammonia molecules around the metallic atom. He refers, in this connexion, to the remarkable fact that polyhydrates of some salts can combine with several molecules of hexamethylenetetramine, and, conversely, compounds of salts with hexamethylenetetramine or caffeine can combine with more water molecules than the salts alone (see A., 1911, i, 184, 266; 1912, i, 812).

That the chemical nature of the anion is not the factor which confers this extra additive capacity on the salt is proved by the fact that the corresponding alkali salts have no affinity for ammonia, and that carboxylates and sulphonates alike give rise to octammines. Additional evidence that the controlling factor is a spatial one is adduced from the fact that salts of dibasic acids, like phthalic and naphthalic acids, do not form octammines, whereas benzoates do.

Even in the aromatic series, however, the experimental material is by no means plentiful, for it so frequently happens that internal complexes are formed between some substituent in the acid and the metallic atom. For example, anomalous results, recognisable by unexpected colours and solubilities of the products, are often met with among halogeno-, amino-, and even ketonic acids.

An unusual phenomenon has been observed in some cases, for example, that of cobalt benzoate octammine, namely, that when once obtained, the ammines are stahle at temperatures much above that at which alone they can be produced.

In the following list of hydrates and ammines, the temperatures given in brackets are those at which the vapour pressures are 760 mm., that is, they are the "dissociation temperatures" on which the author bases his comparisons of stability.

Benzoates.—Nickel; *hexahydrate*, pale green leaflets; *octammine* ($-1·5°$). Cobalt; *tetrahydrate*, grey with a tinge of pink, changes to the bluish-violet anhydrous salt at 115°; *octammine* (32·5°, but can only be prepared at about $-20°$). Copper; the peacock-blue anhydrous salt becomes first violet, then copper-coloured, then dark blue, further greenish-blue and green, and finally forms the grey *octammine* ($-5·5°$); the tensions of the blue *hexammine* (14°), red *tetrammine* (82·5°), and violet *diammine* (183°), are given in place of incorrect data quoted earlier (A., 1916, ii, 104). Manganese; *dihydrate*, very pale pink; *octammine* (10·5°). Zinc; *diammine* (190°), *tetrammine* (57°), *hexammine* (18°), *octammine* ($-2·5°$). Cadmium; *diammine* (182°), *tetrammine* (42°), *hex-*

ammine (17·5°), *octammine* (6°). Ferrous; *trihydrate*, groups of pale green prisms; *octammine* (7°).

Benzenesulphonates.—Nickel; *hexahydrate*, microscopic, rhombic leaflets; *hexammine* (145·5°), bluish-violet. Copper; *hexahydrate*, very pale greenish-blue, silky; *pentammine*, smalt-blue. Zinc; *hexahydrate*, microscopic, rhombic leaflets; *tetrammine* and *pentammine*.

Sulphanilates.—The copper salt is very sparingly soluble, olive-brown when cold, dark brown at 100°, and forms *penta-* and *hexa-ammines* (blue). Nickel; *tetrahydrate*, pale bluish-green prisms; *hexammine* and *octammine* (below 0°), both pale reddish-violet.

Phthalates.—The pale blue copper salt forms a *hexammine*. Nickel; *dihydrate*, brilliant green; *hexammine*.

Trinitrobenzoates.—Copper; *dihydrate*; reddish-brown ammines and an almost black *decammine* (the abnormal additive capacity is partly due to the participation of the nitro-groups).

o-*Naphthoylbenzoates.*—Nickel; *decahydrate*, very pale pink, not green, as most nickel salts; *hexammine* and *octammine* (15°). Copper; *tetra-* and *hexa-hydrates*, almost white; *octammine* (2°). Zinc; *octammine* (−6°).

Naphthalates.—Copper; *tetrahydrate*, slender, pale blue needles; *hexammine* (about 0°) and *tetrammine*, both pale slate-grey. Zinc; *tetrammine*.

a-Naphthalenesulphonates.—Nickel; *trihydrate*, very pale green; *tetra-* and *hexa-ammines*. Copper; *trihydrate*, almost snow-white, although the solution is deep green and the anhydrous salt pale yellowish-brown; *di-* and *tri-ammines*.

β-Naphthalenesulphonates.—Nickel; *nonahydrate*, green; *hexammine*, white; *octammine* (26°), very pale violet. Cobalt; *hexahydrate*, almost colourless; *octammine* (18·5°). Copper; *hexahydrate*, blue; *hexammine* (79·5°); *octammine* (−1°). Zinc; *hexahydrate*, silky leaflets; *octammine* (1·5°). Cadmium; *hexahydrate*; *hexammine* (90·5°). Ferrous; *hexahydrate*, leaflets; *octammine* (−10°). Manganese; *hexahydrate*, almost colourless; *octammine* (3·5°).

Dibromonaphthalene-β-sulphonates.—These are usually so very sparingly soluble that the acid might find application in analysis. Nickel, pearl-grey, forms a *hexammine* (above 150°) and *octammine* (0°). Copper, reddish-violet, forms a *tetrammine*.

Nitroprussides.—Zinc; *trihydrate*; *tetrammine* and *octammine* (−5°). J. C. W.

Hydrogenation of Aromatic Compounds by the Help of Platinum. III. Hydrogenation with Platinum containing Oxygen. Richard Willstätter and Daniel Jaquet (*Ber.*, 1918, **51**, 767—779).—As the application of platinum in the catalytic hydrogenation of organic compounds has developed, various authors have found that it sometimes makes a difference whether the metal is entirely free from oxygen at the commencement of a reduction or has been freely exposed to the air. In many cases, no difference

can be observed, for example, in the reduction of benzene by platinum black (A., 1912, i, 545), but Hess has found that the careful exclusion of oxygen is of great importance in the hydrogenation of pyrrole and certain derivatives (A., 1913, i, 1378). The present paper describes cases of the opposite nature, in which the metal needs to be "primed" occasionally with oxygen, and the conclusion is drawn that platinum itself and platinum loaded with oxygen are distinct catalysts.

A similar difference was observed by Purgotti and Zanichelli (A., 1904, ii, 329), who found that platinum free from air would not induce the decomposition of hydrazine, whilst ordinary platinum preparations will do so, but would cause the decomposition of hydrogen peroxide and hydroxylamine. The particular case now dealt with, however, is the hydrogenation of the anhydrides of *o*-dicarboxylic acids. For example, phthalic anhydride suffers practically no reduction in glacial acetic acid unless the apparatus is opened as occasion requires and the platinum-black is shaken with the air, when the reduction proceeds from stage to stage quite smoothly, the final products being hexahydrophthalide (mixed with a little *o*-hydroxymethylhexahydrobenzoic acid), hexahydro-*o*-toluic acid (a mixture of *cis*- and *trans*-isomerides), and hexahydrophthalic acid. The initial products include phthalide and *o*-toluic acid, which indicates that the anhydride ring is more readily attacked than the benzene nucleus, but in the case of phthalimide, which can only be hydrogenated in glacial acetic acid solution with the best spongy platinum (not necessarily activated by oxygen), the sole product is *hexahydrophthalimide*, $\begin{matrix} CH_2\cdot CH_2\cdot CH\cdot CO \\ CH_2\cdot CH_2\cdot CH\cdot CO \end{matrix}>NH$, monoclinic prisms, m. p. 132°.

Naphthalic anhydride also can only be hydrogenated by platinum which is activated from time to time by oxygen. The products include a tetra- and a deca-hydronaphthalide, decahydroacenaphthene, $C_{12}H_{20}$, and a *tetrahydro-1-methylnaphthalene-8-carboxylic acid*, needles, m. p. 150°.

The influence of such anhydrides on the reduction of the corresponding acids, and even benzene, is remarkable. Unless the precaution of activating the catalyst with oxygen is taken, hydrogenations that would otherwise proceed smoothly are inhibited by traces of these anhydrides. Thus, if phthalic acid is quite free from its anhydride, and naphthalic acid is freshly precipitated from an alkaline solution, they may be reduced to hexa- and tetrahydro-derivatives, respectively, under ordinary conditions, but not otherwise. *iso*Phthalic acid usually contains traces of phthalic anhydride, which inhibits reduction, but may be reduced to a mixture of *cis*- and *trans*-hexahydro-acids if pure and suspended in glacial acetic acid. *p*-Toluic acid readily yields *cis*- and *trans*-hexahydro-acids.

Indole is readily reduced in glacial acetic acid, the final product being *perhydroindole* (*octahydroindole*), which is an alkaline oil with an unpleasant odour, b. p. 182—183°/720 mm., 65°/

12 mm., D_4^{20} 0·9947, and forms a *platinichloride*, m. p. 172—173°, and a *picrate*, m. p. 137—138°. Partial hydrogenation gives a mixture of indole with di- and per-hydroindoles. The perhydroindole may be extracted by shaking the ethereal solution with 0·1*N*-hydrochloric acid, and the other products separated by fractional precipitation with ethereal picric acid. The yellow picrate of the dihydro-base is formed first, and then the red salt of indole itself, and the change in colour is quite distinct at the point of contact of the two liquids. J. C. W.

Acetylaminophenyl Salicylate. Preparation of Salophen. R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 1136—1138).—An investigation of the causes of the poor yields obtained in the preparation of salophen. The reduction of the crude *p*-nitrophenyl salicylate must be effected in non-aqueous solution to prevent hydrolysis of the ester and its reduction product; with glacial acetic acid and zinc dust, the yield of *p*-aminophenyl salicylate is 45% of the theoretical. When this is acetylated without being isolated, the yield of crude salophen, m. p. 175—180°, is 60% of the theoretical.

Using purified *p*-nitrophenyl salicylate, the yield of *p*-aminophenyl salicylate is increased to 73%, and that of salophen to 80%, of the theoretical. [See *J. Soc. Chem. Ind.*, 1918, 530A.] C. S.

A New Group of *cyclo*Propane Derivatives. II. Action of some Analogues of Phenacyl Haloids on 3-Acylcoumarins. OSKAR WIDMAN (*Ber.*, 1918, **51**, 907—911. Compare this vol., i, 347).—The reaction described in the first paper is found to be common to other aryl halogenomethyl ketones.

Thus, *p*-chloroacetylanisole (*p*-methoxyphenyl chloromethyl ketone) reacts with 3-acetylcoumarin in the presence of sodium ethoxide to form 3-*acetyl*-3:4-*anisacylidenecoumarin*,

$$\begin{array}{l} C_6H_4{-}CH{-} \\ O{\cdot}CO{\cdot}CAc \end{array}\!\!>CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

which crystallises in long needles, m. p. 163°, and *ethyl* α-*acetyl*-αβ-*anisacylidenecoumarinate* [*ethyl* 1-*acetyl*-2-p-*methoxybenzoyl*-3-o-*hydroxyphenyl*cyclo*propane*-1-*carboxylate*],

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH\!<\!\begin{array}{l} CAc{\cdot}CO_2Et \\ CH{\cdot}C_6H_4{\cdot}OH \end{array},$$

which separates from benzene in long, flat prisms with $1C_6H_6$, m. p. 70°, or 119—120° when free from solvent benzene.

3-Benzoylcoumarin yields 3-*benzoyl*-3:4-*anisacylidenecoumarin*, long, pointed prisms, m. p. 190°, whilst ethyl coumarin-3-carboxylate forms *ethyl* 3:4-*anisacylidenecoumarin*-3-*carboxylate*, prisms, m. p. 165—166°, and *ethyl* 2-p-*methoxybenzoyl*-3-o-*hydroxyphenyl*cyclo*propane*-1:1-*dicarboxylate*, m. p. 99—100°.

The ethyl 3:4-anisacylidenecoumarin-3-carboxylate is hydrolysed

by 4% sodium hydroxide to *α-hydroxy-γ-p-methoxybenzoyl-α-o-hydroxyphenylpropane-ββ-dicarboxylic acid*,

$OH \cdot C_6H_4 \cdot CH(OH) \cdot C(CO_2H)_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OMe$,

short prisms, m. p. 119—120°, and *anisacylmalonic acid*,

$OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH(CO_2H)_2$,

which crystallises in stellate groups of needles, m. p. 162° (decomp.), and may be synthesised by condensing *p*-chloroacetylanisole with ethyl sodiomalonate.

o-Chloroacetylanisole yields *3-acetyl-3 : 4-o-methoxyphenacylidene-coumarin*, prisms, m. p. 144—145°; ω-bromo-*m*-nitroacetophenone gives rise to *ethyl 3 : 4-m-nitrophenacylidenecoumarin-3-carboxylate*, prisms, m. p. 162—163°, and *ethyl 2-m-nitrobenzoyl-3-o-hydroxyphenylcyclopropane-1 : 1-dicarboxylate*, large, hard crystals, m. p. 132—133°; and 1-chloroacetylnaphthalene (α-naphthyl chloromethyl ketone, b. p. 204—205°/18 mm.) produces *3-acetyl-3 : 4-α-naphthacylidenecoumarin*, hard prisms, m. p. 133—134°.

J. C. W.

Some New Derivatives of *p*-Coumaric and Vanillic Acids. Fritz von Konek and Eugen Pacsu (*Ber.*, 1918, **51**, 855—865).—Some years ago, Konek synthesised methyl 3-amino-6-benzoyloxybenzoate hydrochloride and found that it had a cocaine-like effect (*Math.-Naturwiss. Anz. Akad. Wiss., Budapest*, **14**, 16). The synthesis has now been extended to other phenolic acids in order to test the influence of the kind and position of the various groups on the physiological activity.

p-Coumaric (*p*-hydroxycinnamic) acid, from *p*-hydroxybenzaldehyde by Perkin's method, is converted into the methyl ester, and this is treated with *p*-nitrobenzoyl chloride and sodium hydroxide solution. The *methyl p-4′-nitrobenzoyloxycinnamate*, rosettes of silky, white needles, m. p. 203°, is reduced by means of tin and alcoholic hydrogen chloride to *methyl p-4′-aminobenzoyloxycinnamate*, $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot C_6H_4 \cdot CH:CH \cdot CO_2Me$, which has m. p. 168—169°, and forms a very sparingly soluble *hydrochloride*, long needles, decomp. 215°, and sulphate.

For the preparation of another ester, β-*p*-nitrophenylpropionic acid was required. This is prepared as follows: β-phenylpropionic acid (hydrocinnamic acid) is dissolved in about ten times its weight of fuming nitric acid at 85°, the solution is poured into ice-water, and the crude product dissolved in about fifty times its weight of boiling water and then cooled to 65°, whereby the *p*-nitro-acid separates almost pure, leaving the *o*-nitro-acid to crystallise on cooling further. About 63% of the parent acid is converted into the para-derivative and 30% into the ortho-compound by this means. The desired acid is treated with thionyl chloride, and the *β-p-nitrophenylpropionyl chloride*, b. p. 189—192°/16 mm., m. p. 34—35°, is treated with methyl *p*-hydroxycinnamate, whereby *methyl p-β-4′-nitrophenylpropionoxycinnamate* is formed, in white needles, m. p. 131—132°. This is reduced to *methyl p-β-4′-aminophenylpropionoxycinnamate*,

$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot C_6H_4 \cdot CH:CH \cdot CO_2Me$,

which crystallises in long needles, m. p. 153—154°, and forms a sparingly soluble *hydrochloride*, decomp. 250°.

5-Nitrovanillic acid (Vogl, A., 1899, i, 697) is converted by means of thionyl chloride into the chloride, *5-nitro-4-hydroxy-3-methoxybenzoyl chloride*, m. p. 93—94°, this into the *methyl* ester, pale yellow, glistening needles, m. p. 148—149°, and then into *methyl 5-nitro-4-benzoyloxy-3-methoxybenzoate*, pale yellowish-brown needles, m. p. 124—125°, by means of benzoyl chloride and pyridine. This ester is reduced to *methyl 5-amino-4-benzoyloxy-3-methoxybenzoate*, $OBz\cdot C_6H_2(NH_2)(OMe)\cdot CO_2Me$, which crystallises in needles, m. p. 188—190°, and forms a sparingly soluble *hydrochloride*, decomp. 236—240°.

Neither of the above amino-acid esters has any effect on the epidermis or tongue. J. C. W.

Some Piperylhydrazones. ALBERT WEINHAGEN (T., 1918, **113**, 585—587).—A description of the condensation products of several aldehydes and ketones with piperylhydrazine, the latter being obtained by the reduction of nitrosopiperidine.

Piperonalpiperylhydrazone, $C_{13}H_{16}O_2N_2$, forms colourless needles, m. p. 65—67°; *salicylaldehydepiperylhydrazone*, $C_{12}H_{16}ON_2$, needles, rhombic plates, or octahedra, m. p. 71—72°; *formaldehydepiperylhydrazone*, $C_6H_{12}N_2$, prismatic needles, m. p. 78—79°; benzaldehydepiperylhydrazone, pentagonal or hexagonal plates, m. p. 68—69° (compare Forster, T., 1915, **107**, 267); *anisaldehydepiperylhydrazone*, $C_{13}H_{18}ON_2$, hexagonal plates, m. p. 54°; p-*hydroxybenzaldehydepiperylhydrazone*, $C_{12}H_{16}ON_2$, m. p. 161°; p-*aminoacetophenonepiperylhydrazone*, $C_{13}H_{19}N_3,H_2O$, prismatic crystals, m. p. 108°. With *iso*valeraldehyde, a small quantity of a *substance*, m. p. near 122°, was obtained, whilst with propionaldehyde, acetone, *p*-aminobenzaldehyde, dextrose, galactose, and *l*-xylose the products were resinous. D. F. T.

Attempt to Synthesise Fisetol. J. TAMBOR and EDMOND M. DU BOIS (*Ber.*, 1918, **51**, 748—751).—*m*-Dimethoxybenzene is condensed with bromoacetyl bromide under the influence of aluminium chloride, and thus converted into *2-hydroxy-4-methoxyphenyl bromomethyl ketone* (*ω-bromoresacetophenone methyl ether*), $OH\cdot C_6H_3(OMe)\cdot CO\cdot CH_2Br$, which crystallises in stout prisms, m. p. 92° (compare A., 1905, i, 916, and Auwers and Pohl, A., 1914, i, 981). The corresponding *chloro-compound* forms white needles, m. p. 119°, and the *iodo*-derivative separates in very pale yellow prisms, m. p. 102°. If the bromo-ketone is heated with sodium acetate and acetic anhydride, it yields the *diacetate* (glistening scales, m. p. 86°) of *2-hydroxy-4-methoxyphenyl hydroxymethyl ketone*, this being obtained in colourless plates, m. p. 128°, by hydrolysis with alcoholic potassium hydroxide. The latter is the methyl ether of fisetol, but no method has been devised whereby the methoxyl group can be exchanged for hydroxyl. J. C. W.

Pungent Principles of Ginger. I. Zingiberone. (A Correction.) Hiroshi Nomura (*Sci. Rep. Tohôku Imp. Univ.*, 1918, **6**, 375).—The ketone, isolated from ginger, to which, in a previous paper (*ibid.*, 1917, **6**, 41), the name zingiberone was assigned, bears no relation to the zingiberol obtained by Brooks (A., 1916, i, 408), and in order to avoid confusion the name zingerone is substituted for zingiberone (compare T., 1917, **111**, 769; Lapworth, Pearson, and Royle, *ibid.*, 777). H. M. D.

Oxidation of Diaminophenols. Jean Piccard and Louis M. Larsen (*J. Amer. Chem. Soc.*, 1918, **40**, 1079—1092).—Holoquinonoid aminobenzoquinoneimine salts have been prepared with the purpose of comparing their colours with those of other holoquinonoid and of meriquinonoid salts. It is found that the auxochromic effect of an anilino-group is, unlike the cases of other holoquinonoid salts, the same as that of a dimethylamino-group. *2-Amino-p-benzoquinone-4-imine hydrochloride*,

$$O:C_6H_3(NH_2):NH,HCl,$$

which separates when an aqueous solution of 2:4-diaminophenol dihydrochloride is oxidised by 4*N*-ferric chloride at 0°, and the solution is further cooled to −15°, crystallises in two forms, unstable, pale red needles and stable, dark red plates with a green surface colour; it is rapidly decomposed by water, is proved to be holoquinonoid by titration with titanium trichloride, forms red solutions in water or alcohol, which are changed to yellow by concentrated sulphuric acid owing to salt-formation at the amino-group, and gives a spectrum showing general absorption in the violet region. The quinonoid *perchlorate* was obtained in pale red needles (not quite pure) which exploded violently when heated. The quinonoid *nitrate* was obtained by oxidising with 2*N*-ferric nitrate instead of with 4*N*-ferric chloride; it is more stable than the hydrochloride and exists in only one modification, bright red needles. *2-Dimethylamino-p-benzoquinone-4-imine perchlorate*, $O:C_6H_3(NMe_2):NH,HClO_4$, is obtained by oxidising 4-amino-2-dimethylaminophenol dihydrochloride with 4*N*-ferric chloride at 0°, adding a saturated solution of sodium perchlorate, and cooling to −20°; it crystallises in pale red needles which slowly darken on keeping, forms violet-red solutions, is unchanged by strong acids except concentrated sulphuric acid, in which it dissolves to a pale yellow solution, becoming violet-red again on dilution, and gives a flat absorption curve with a wide maximum in the green. The *picrate* crystallises in long, dark brown needles, and forms red solutions in alcohol and acetone.

3-Amino-6-hydroxydiphenylamine, colourless crystals which rapidly oxidise in air, obtained by the electrolytic reduction of *m*-nitrodiphenylamine in concentrated sulphuric acid (1·5 amps., 6·5 volts, electrode 15 sq. cm.), is isolated as the *dihydrochloride*, unstable, hygroscopic crystals, which in 50% acetic acid at 0° is oxidised by 4*N*-ferric chloride, the addition of picric acid in glacial acetic acid to the resulting violet solution yielding *2-anilino-p-*

enzoquinone-4-imine picrate, $O:C_6H_3(NHPh):NH,C_6H_2(NO_2)_3\cdot OH$. This salt forms a microcrystalline powder, yields red solutions in alcohol and acetone, and dissolves in dilute acids, forming violet solutions. Salts with the usual inorganic acids have not been obtained, on account of their instability in solution.

An orthoquinonoid structure of the preceding quinoneimine salts is not impossible. C. S.

Syntheses by Means of Sodamide. Preparation and Study of some Monoalkyl and Dialkylcamphors and their Derivatives. A. HALLER and JEAN LOUVRIER (*Ann. Chim.*, 1918, [ix], **9**, 189—251).—For the most part a more detailed account of work already published (compare A., 1914, i, 555). The following new compounds are described. *Diethylcampholamide*, m. p. 75°, b. p. 185°/12 mm., $[\alpha]_D^{18}$ +76°15′ to 77°5′, prepared by the action of sodamide on diethylcamphor in xylene, when acted on by nitrous acid yields *diethylcampholic acid*, m. p. 78°, b. p. 157°/20 mm., $[\alpha]_D^{15}$ +60°59′ to 62°49′, giving a *potassium* salt. *Methylethylcampholamide*, m. p. 60°, b. p. 180°/14 mm., $[\alpha]_D^{15}$ +75°42′ to 73°55′, yields *methylethylcampholic acid*, m. p. 74°, $[\alpha]_D^{15}$ +57°10′ to 55°24′.

Allylborneol, b. p. 119°/14 mm., $[\alpha]_D^{16}$ +19°23′ to 20°22′, gives a *phenylurethane*, m. p. 64°.

Diallylcamphor, b. p. 155°/16 mm., D_0^0 0·982, $[\alpha]_D^{17}$ +148° to 152°22′; *diallylborneol*, m. p. 47°, $[\alpha]_D^{18}$ +78°28′; *diallylcampholamide* or 4(2′ : 2′ : 3′)-*trimethyl*cyclo*pentyl-2-methyl-4-allylpyrrolidone*, $NH_2\cdot CO\cdot C_8H_{14}\cdot CH(C_3H_5)_2$ or

$$NH\!<\!\begin{matrix}CHMe\cdot CH_2\\ CO\text{———}C(C_3H_5)\cdot CH\!<\!\begin{matrix}CMe_2\cdot CHMe\\ CH_2\text{—}CH_2\end{matrix}\end{matrix}.$$

b. p. 212°/15 mm., $[\alpha]_D^{18}$ 40°18′.

Dibenzylcampholamide, m. p. 121°, $[\alpha]_D^{19}$ +33°7′ to 34°18′.

Benzylethylcampholamide, m. p. 181°, b. p. 230—240°/12 mm.

Ethylcampholenonitrile, b. p. 110°/11 mm., D_0^0 0·903, $[\alpha]_D^{13}$ +70°26′, gives in turn *ethylcampholenamide*, m. p. 62°, and *ethylcampholenic acid*, m. p. 36°, b. p. 157°/20 mm.

Allylcamphoroxime, m. p. 101°, b. p. 158°/16 mm., $[\alpha]_D^{14}$ +58°10′ to 54°14′, gives a *phenylurethane*, m. p. 160°, and yields in turn *allylcampholenonitrile*, b. p. 130°/11 mm., D_0^0 0·934, $[\alpha]_D^{14}$ +28°47′; *allylcampholenamide*, m. p. 97°; and *allylcampholenic acid*, m. p. 49°, b. p. 156°/16 mm.

Propylcamphoroxime yields *propylcampholenonitrile*, b. p. 124°/11 mm., D_0^0 0·907, $[\alpha]_D^{16}$ +46°18′; *propylcampholenamide*, b. p. 173°/12 mm.; and *propylcampholenic acid*, b. p. 160°/12 mm.

Benzylcamphoroxime gives *benzylcampholenonitrile*, b. p. 195°/14 mm., $[\alpha]_D^{17}$ +54°14′ to +43°58′, according to the method of preparation; *benzylcampholenamide*, b. p. 197°/12 mm., and *benzylcampholenic acid*, m. p. 68°, b. p. 204°/12 mm., which gives a *sodium* salt. W. G.

The Wagner Rearrangement. L. Ruzicka (*Helvetica Chim. Acta*, 1918, **1**, 110—133).—It is shown that whilst methyl-α-fenchocamphorol and methylcamphenilol apparently do not undergo the Wagner rearrangement when heated with sodium hydrogen sulphate, methylborneol and methylfenchyl alcohol, despite their marked difference in structure, give the same reaction products after the removal of water, namely, fenchone aud camphor. These results go to show that of the two possible explanations of the Wagner rearrangement, that demanding the intermediate formation of a tricyclene ring is the more correct. The apparent contradiction underlying this explanation can be elucidated in the following way, and a further proof of the tricyclene theory advanced at the same time. Whereas the tricyclenes derived from borneol and fenchyl alcohol are different substances, it is found that the tricyclenes obtained from their homologues, methylborneol and methylfenchyl alcohol, must be identical. It is therefore clear that in this case the further products of the reaction must also be identical. The formation of this common tricyclene from compounds of the fenchone and camphor types is to be attributed to the fact that the single linkings of the tricyclene three-membered ring exhibit different stabilities towards sodium hydrogen sulphate. Generally, the linking which leads to the fenchone type is opened, whilst that leading to the camphor type is more stable; the third linking, which would lead to an unknown type, is not opened. A consideration of the tricyclenes obtainable from the other alcohols shows that otherwise quite different isomeric alcohols yield the same tricyclene. This will explain why methylcamphenilol apparently does not undergo rearrangement on removing water. The tricyclene obtained is identical with that furnished by borneol, and consequently the only product of the reaction is camphene. With regard to the further rupture of the three-membered ring of the tricyclene, the author gives the following generalisations:

(1) Of the linkings of the three-membered ring of the tricyclenes, that is the weakest which lies between the two carbon atoms where the difference between the numbers of directly connected hydrogen atoms is greatest.

(2) Should two bonds be similar in the above respect, then that one will be opened which at the same time opens the five-membered ring with the largest number of quaternary carbon atoms.

A number of tables showing the relationships are included in tbe paper. J. F. S.

Constituents of Resins. I. Siaresinol from Siamese Gum Benzoin. Alois Zinke and Hans Lieb (*Monatsh.*, 1918, **39**, 95—105).—Siaresinol from Siamese gum henzoin (Reinitzer, A., 1915, i, 431) is probably identical with the benzoresinol obtained by Lüdy from the same source (A., 1893, i, 666); it gives an *additive* compound with acetic acid, $C_{30}H_{48}O_4,C_2H_4O_2$, needles, m. p. 280—281·5°, and a *benzoyl* derivative, needles, m. p.

182—183°, $[\alpha]_D^{20}$ +30·0° (ethyl alcohol), which on hydrolysis regenerates siaresinol. D. F. T.

The Isolation of Pigments by Means of Picric and Dichloropicric Acids. RICHARD WILLSTÄTTER and GUSTAV SCHUDEL (*Ber.*, 1918, **51**, 782—788).—*In devising a method for the extraction of plant pigments,* Willstätter has already had a certain measure of success with a process which depends on the partition of the dye between water and amyl alcohol (compare A., 1917, i, 42—50). The serious limitation to this method is that only non-glucosidic pigments are efficiently extracted, diglucosides often being left entirely in the aqueous layer. If picric acid is added to the solution, a wider range of pigments can be transferred, as picrates, to other, non-miscible solvents. Thus, ether will only dissolve the picrates of non-glucosidic pigments; diethyl ketone will not remove the diglucoside picrates, but extracts monoglucoside picrates to the extent of about 50% of the quantity present; whilst a mixture of amyl alcohol (2 parts) and acetophenone (1 part) will remove all the monoglucosides and 70—80% of the diglucosides as picrates.

The use of picric acid has this drawback, however, that the picrates are usually not very soluble in organic media. Dichloropicric acid is much superior in this respect, although it is so much more soluble in water that the expenditure of reagent is greater. By the use of this acid, rosaniline and pararosaniline can be completely extracted from aqueous solutions by ether; safranine by diethyl ketone; methylene-blue by ether, the picrate crystallising soon in bronzy prisms; and mono- and di-glucosidic pigments can be removed completely by one extraction with a mixture of amyl alcohol and acetophenone (2:1).

No actual example of the use of dichloropicric acid is given, but the occasion serves to describe its preparation. *p*-Nitroaniline is chlorinated by Flürscheim's method (T., 1908, **93**, 1772), the 2:6-dichloro-4-nitroaniline is converted into 3:5-dichloro-1-nitrobenzene (Holleman, A., 1905, i, 41), and this is reduced to the amine by means of iron filings and hydrochloric acid, and then transformed into 3:5-dichlorophenol, which is nitrated by means of fuming nitric acid and acetic acid. Dichloropicric acid (3:5-dichloro-2:4:6-trinitrophenol) crystallises in pale yellow prisms, m. p. 139—140° (corr.) (compare Blanksma, *Rec. trav. chim.*, 1908, **27**, 25, 36), the sodium salt in quadratic prisms, and the potassium salt in slender needles, both being lemon-yellow. The solubilities in water at 19·7° are 7·4, 7·4, and 0·55 grams per 100 c.c., for the acid, Na and K salt, respectively.

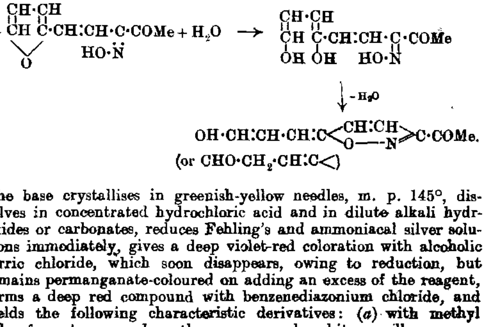
The conversion of 3:5-dichloroaniline into 3:5-dichlorophenol is carried out by adding the solution of the diazonium sulphate to a boiling mixture of concentrated sulphuric acid, water, and anhydrous sodium sulphate (proportions, 9:5:6). If Blanksma's method is adopted (*ibid.*), the following by-products arise: 3:5-

dichloro-4-3′:5′-dichlorobenzeneazophenol, brownish-red, flat, silky prisms, m. p. 191—192° (corr.), and 3:5-*dichloro-2:4-bis-3′:5′-dichlorobenzeneazophenol*, $OH\cdot C_6HCl_2(N\colon N\cdot C_6H_3Cl_2)_2$, long, glistening, orange needles, m. p. 260—261° (corr.), both of which form sodium salts which dissolve in ether; and 3:5-*dichloro-4-nitrosophenol*, very pale greenish-yellow prisms, m. p. 150—151° (corr.).

J. C. W.

Isomerism of Furfurylidenediacetyl Monoxime [β-2-Furylvinyl Acetyl Ketoxime]. OTTO DIELS and HERMANN ROEHLING (*Ber.*, 1918, **51**, 828—836. Compare A., 1913, i, 875).—The product of the condensation of furfuraldehyde with dimethyl diketone monoxime, namely, β-2-furylvinyl acetyl ketoxime, yields an *acetate*, $C_4H_3O\cdot CH\colon CH\cdot CAc\colon N\cdot OAc$, prisms, m. p. 141°, which is transformed by warming with 33% potassium hydroxide into the salt of β-2-furylacrylic acid, $C_4H_3O\cdot CH\colon CH\cdot CO_2H$.

When added to concentrated hydrochloric acid, the oxime rapidly dissolves with a deep olive-green colour, changing to brown, and then deposits crystalline leaflets of the *hydrochloride*, decomp. 128—129°, of an isomeric *base*, which is supposed to be formed by the hydrolytic rupture of the furan ring, followed by ring closure in a new position, thus:



The base crystallises in greenish-yellow needles, m. p. 145°, dissolves in concentrated hydrochloric acid and in dilute alkali hydroxides or carbonates, reduces Fehling's and ammoniacal silver solutions immediately, gives a deep violet-red coloration with alcoholic ferric chloride, which soon disappears, owing to reduction, but remains permanganate-coloured on adding an excess of the reagent, forms a deep red compound with benzenediazonium chloride, and yields the following characteristic derivatives: (*a*) with methyl chloroformate, a *carbomethoxy*-compound, white needles, m. p. 128—129°; (*b*) a p-*nitrophenylhydrazone*, brownish-red, slender, curved needles, decomp. 136—137°; (*c*) with methylamine, a *product*, $C_{10}H_{12}O_2N_2$, pale yellow needles, m. p. 175° (decomp.), and a substance crystallising in stout, chromate-red rhombohedra, m. p. 183°. When boiled with an excess of water or dilute sulphuric acid, or heated with methyl iodide at 100°, the base changes into a third isomeride, namely, 3-*acetyl*-5-2′-*furyl*-4:5-

dihydroisooxazole, $C_4H_3O\cdot CH<\begin{matrix}CH_2\cdot CAc\\ O—N\end{matrix}$, which crystallises in soft, white needles, m. p. 103—104°. J. C. W.

β-Phenylcoumarins. ADOLF SONN (*Ber.*, 1918, **51**, 821—827). —Some years ago, von Meyer stated that 3-hydroxyflavone is produced when benzoacetodinitrile, $NH:CPh\cdot CH_2\cdot CN$, is condensed with resorcinol under the influence of hydrogen chloride (A., 1903, i, 482). It is known that dinitriles of this type readily change into acylacetonitriles on treatment with acids, and therefore it might be expected that the above result would be achieved if ω-cyanoacetophenone, $COPh\cdot CH_2\cdot CN$, were substituted for the dinitrile. Bargellini and Forli-Forti have already studied the condensation of compounds of this type with phenols, and proved that the products are β-phenylcoumarins and not flavones. This led the author to suspect that von Meyer had wrongly interpreted his result, and he has found, on repeating the experiment, that the product is not 3-hydroxyflavone, but 7-hydroxy-4-phenylcoumarin (Pechmann and Hancke, A., 1901, i, 210).

In their condensations, Bargellini and Forli-Forti used zinc chloride, and were not very successful. It is better to dissolve the materials in glacial acetic acid and to employ hydrogen chloride as the condensing agent. Thus, *p*-cyanoacetylanisole and phloroglucinol yield 5 : *7-dihydroxy-4-p-methoxyphenylcoumarin*, which crystallises in flat prisms, m. p. 262°, and forms a *diacetate*, glistening, elongated tablets or flat prisms, m. p. 189—190° (the Italian authors gave m. p. 179—180°). If ether is used as solvent, a different product is formed, most probably the corresponding *imino-ether*, $C_6H_2(OH)_2<\begin{matrix}O——————C:NH\\ C(C_6H_4\cdot OMe):CH\end{matrix}$, stout, pale yellow crystals, decomp. above 300°, since it yields the coumarin on warming with water or dilute acids.

The dinitrile corresponding with *p*-cyanoacetylanisole, namely, *p-methoxybenzimidoacetonitrile*, $OMe\cdot C_6H_4\cdot C(:NH)\cdot CH_2\cdot CN$, is obtained in colourless, stout prisms, m. p. 119°, by the interaction of anisonitrile and acetonitrile in the presence of sodium, the primary sodium salt being decomposed by water. J. C. W.

Synthesis of Ketones in the Thiophen Series. V. THOMAS and V. COUDERC (*Bull. Soc. chim.*, 1918, [iv], **23**, 288—291).—Magnesium thienyl iodide reacts with nitriles, giving products which when treated with water give good yields of ketones. The following have been prepared by this method: ethyl thienyl ketone: phenyl thienyl ketone, dithienyl ketone; *α-naphthyl thienyl ketone*, b. p. 187—188°/25 mm.; and *β-naphthyl thienyl ketone*, colourless needles, m. p. 87°. W. G.

Synthesis of 1-Methyltetrahydropyridinecarboxylic Acids. I. A New Method for Preparing Arecaidine and Arecoline. Elucidation of the Constitution of Guvacine and Arecaine. KURT HESS and FRIEDRICH LEIBBRANDT (*Ber.*, 1918, **51**, 806—820). —When the 1-methylpiperidinecarboxylic acids are brominated in

methyl or ethyl alcohol and the products are heated with sodium alkyl oxides, 1-methyltetrahydropyridinecarboxylic acids are produced. These are closely related to the alkaloids of the areca (betel) nut.

Nipecotinic acid (piperidine-3-carboxylic acid) forms a fairly stable *acetate*, needles, m. p. 289—290° (decomp.). The following new derivatives of 1-methylpiperidine-3-carboxylic acid (compare A., 1917, i, 354) have been prepared: from the methyl ester (dihydroarecoline), the *hydrochloride*, needles, m. p. 193° (decomp.); methiodide, prismatic plates, m. p. 192°; and methoaurichloride, m. p. 123° (compare Willstätter, A., 1897, i, 385); also the *ethyl* ester, b. p. 101—102°/24 mm., and green *copper* salt.

Methyl 1-methylpiperidine-3-carboxylate is converted as indicated above into methyl 1-methyl-1 : 2 : 5 : 6-tetrahydropyridine-3-carboxylate, which is identical with arecoline, as the corresponding free acid is identical with arecaidine. The latter forms a *hydrobromide*, needles, m. p. 197° (decomp.).

Two other areca-nut alkaloids have been registered, namely, guvacine and its *N*-methyl derivative, arecaine (Jahns, A., 1891, 94, 1520). Assuming that these must be closely related to arecaidine, the authors have prepared 1-methyl-1 : 4 : 5 : 6-tetrahydropyridine-2-carboxylic acid from 1-methylpiperidine-2-carboxylic acid in the same way. This very closely resembles, but is not identical with, arecaine. *Methyl 1-methylpiperidine-2-carboxylate*, from pipecolinic acid acetate (*loc. cit.*), has b. p. 92—95°/21 mm., and the *hydrochloride* of the ethyl ester (*ibid.*) has m. p. 204° (decomp.). 1-*Methyl*-1 : 4 : 5 : 6-*tetrahydropyridine-2-carboxylic acid* crystallises from pure alcohol in well-developed, quadratic, prismatic tablets, m. p. 213—214° (arecaine is insoluble in alcohol and has m. p. 231°), and forms a *hydrochloride*, m. p. 210°, readily soluble in alcohol (arecaine hydrochloride has m. p. 250° and is sparingly soluble), a *platinichloride*, orange-yellow prisms, m. p. 220° (arecaine platinichloride forms octahedra), an *aurichloride*, m. p. 200°, a *methyl* ester, and an *ethyl* ester, b. p. 96°/17 mm., both of which are limpid, highly refractive, pleasant-smelling oils.

The relationship between guvacine and arecaine is definitely established by methylating the former by the author's method, using formaldehyde and formic acid. The pure arecaine and its salts thus obtained had somewhat different properties from those quoted by Jahns; the new data are given above in brackets. When arecaine is boiled with alcoholic hydrogen chloride, it loses its methyl group and forms the *ethyl* ester of guvacine, b. p. 116°/19 mm., instead of its own ethyl ester. This oil reduces alkaline permanganate and absorbs bromine immediately.

This esterification of arecaine proves one thing, however, namely, that a carboxyl group is present in these alkaloids. That they also contain an ethylene linking is proved by the reduction of guvacine with hydrogen and colloidal platinum, when "dihydroguvacine" is formed. This is identical with *iso*nipecotinic acid (piperidine-4-carboxylic acid). Consequently, guvacine is a tetrahydro-

pyridine-4-carboxylic acid, probably the 1:2:5:6-isomeride, and arecaine is its 1-methyl derivative. J. C. W.

Guvacine Methyl Ester (Guvacoline) and its Occurrence in Nature. KURT HESS (*Ber.*, 1918, **51**, 1004—1006).—The alkaloids of the areca nut include arecaidine and its methyl ester, arecoline, guvacine and its *N*-methyl derivative, arecaine, and also the methyl ester of guvacine, which is designated "*guvacoline*." A specimen of the *hydrobromide* of this, crystallising in short prisms, m. p. 144—145°, has been provided by Messrs. Merck, and proved to have the above constitution by hydrolysis to guvacine and by esterification of this alkaloid. J. C. W.

Guvacine. KARL FREUDENBERG (*Ber.*, 1918, **51**, 976—982).—Independent of Hess, and without reference to his work (preceding abstracts), the author has investigated guvacine, and draws the conclusion that it is demethylated arecaidine, or 1:2:5:6-tetrahydropyridine-3-carboxylic acid. If this is so, then arecaine and arecaidine are identical.

The above acid was synthesised by Wohl and Losanitsch (A., 1908, i, 47), and there is good agreement between the decomposition temperatures of the hydrochlorides, aurichlorides, and platinichlorides of this and guvacine. Guvacine *methyl ester*, b. p. 114° (corr.)/13 mm., forms a *hydrochloride*, hygroscopic leaflets, m. p. 121—122° (corr.), a *platinichloride*, silky, golden leaflets, m. p. 211° (corr.), and a methiodide. The latter has the same m. p. as arecoline methiodide, and yields arecaidine on hydrolysis, there being again good agreement in the decomposition temperatures of the salts of the natural alkaloid and the present material.

1-p-*Toluenesulphonylguvacine* crystallises in stout plates, m. p. 167—168° (corr.), and is oxidised by alkaline permanganate to a (3 : 4 ?)-*dihydroxy*-1-p-*toluenesulphonylpiperidine*-(3 ?)-*carboxylic acid*, leaflets, m. p. 213—214° (corr.; decomp.), and by ozone in 95% acetic acid to a dicarboxylic *acid*, probably of the formula $C_7H_7\cdot SO_2\cdot N<\begin{matrix}CH_2\cdot CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$, which crystallises in prisms and plates, m. p. 164° (corr.). J. C. W.

A New Volatile Alkaloid of the Common Broom. AMAND VALEUR (*Compt. rend.*, 1918, **167**, 163—164. Compare this vol., i, 350).—After separation of the alkaloids sparteine and sarothamnine (*loc. cit.*) from the mother liquors in the manufacture of sparteine sulphate, a new alkaloid was obtained by the addition of excess of alkali and extraction with ether. The new alkaloid, *genisteine*, $C_{16}H_{28}N_2$, has m. p. 60·5°, b. p. 139·5—140·5°/5 mm. (corr.), 177—178°/22 mm. (corr.), and yields a *hydrate*,

$$C_{16}H_{28}N_2,H_2O,$$

$[\alpha]_D$ −52·3° (in alcohol), a *picrate*, $C_{16}H_{28}N_2,2C_6H_2(NO_2)_3\cdot OH$, m. p. 215° (decomp.), a *platinichloride*,

$$C_{16}H_{28}N_2,2HCl,PtCl_4,2\tfrac{1}{2}H_2O;$$

decomposing at 235°, and an *aurichloride*,

$2(C_{16}H_{28}N_2,2HCl),3AuCl_3$,

yellow prisms, m. p. 188° (decomp.). This alkaloid is saturated and does not contain a methyl group attached to nitrogen.

W. G.

The Alkaloids of the Pomegranate Tree. V. Resolution of Pelletierine and Methyl*iso*pelletierine into their Optical Antipodes. Elucidation of Tanret's Bases. KURT HESS and ANNALIESE EICHEL (*Ber.*, 1918, **51**, 741—747. Compare this vol., i, 34).—Pelletierine and methyl*iso*pelletierine have been resolved by means of their tartrates. The bases were first treated with the *d*-acid, the solutions evaporated in a vacuum desiccator to syrupy consistency, and then mixed with alcohol, when the salt of the *d*-base separated, and then the *l*-base was recovered from the mother liquor and converted into the *l*-tartrate.

d-*Pelletierine* d-*tartrate* has m. p. *129°*, $[\alpha]^{20}$ + *19·48°*, and l-*pelletierine* l-*tartrate* has m. p. 129°, $[\alpha]^{20}$ − 19·62°. The active bases suffer considerable racemisation on distillation, but they may be isolated and converted into solutions of their sulphates with constant rotation, $[\alpha]^{18}$ + 5·39° and − 5·33° respectively. d-*Methyl-isopelletierine* d-*tartrate* has m. p. 133—134°, $[\alpha]^{20}$ + 19·12°, and l-*methylisopelletierine* l-*tartrate* has m. p. 132—134°, $[\alpha]^{18}$ − 19·37°. The free bases, in this case, are not subject to racemisation when distilled, resembling in this respect the parent alkaloid, coniine. The difference is probably due to the position of the oxygen atom, the side-chain being $-CH_2·CH_2·CHO$ in the case of pelletierine and $-CO·CH_2·CH_3$ in the other case. d-*Methylisopelletierine* has b. p. 109°/24 mm., $[\alpha]^{18}$ + 6·71° (solution in *N*-sulphuric acid), + 9·90° (solution in hydrochloric acid), and the l-*base* has practically the corresponding constants. (The light employed was that of an incandescent gas lamp.)

Among the alkaloids of the pomegranate, Tanret described some optically active forms of the above bases, but the rotations reported by him were much greater than those observed with the resolved alkaloids. The authors feel quite convinced that no active modifications are present in the root, for they have not found optical activity to be displayed by any of their fractions, either before or after distillation.

J. C. W.

Degradation of Scopoline. III. Scopoline → Hydroscopoline → Tropan. KURT HESS (*Ber.*, 1918, **51**, 1007—1015. Compare A., 1916, i, 285, and Schmidt, *ibid.*).—It has been suggested already that hydroscopoline is a dihydroxytropan. Hydroxytropans are found to resist reduction by ordinary methods, but when heated with concentrated hydriodic acid and a considerable excess of phosphonium iodide at 200°, they suffer replacement of hydroxyl by hydrogen fairly readily. Thus tropine yields tropan and nortropine gives nortropan, whilst hydroscopoline also forms tropan, which supports the above assumption.

Of the two oxygen atoms in scopoline, one is known to be present in a hydroxyl group and the other is probably included in an oxide ring. The comparative ease with which scopoline combines with hydrogen bromide and parts with it again on treatment with alkalis suggests the oxidic structure, but there can scarcely be an ethylene-oxide arrangement such as Schmidt proposed, thus,

$$\begin{matrix}-C\cdot OH \\ \quad >O \\ -CH\end{matrix}$$

, as a hydrogen bromide additive compound from this would be very unstable, which hydroscopoline bromide is not. The author believes that the oxygen atom in question bridges across from the pyrrolidine ring to some carbon atom in the piperidine ring.

When hydroscopoline bromide hydrobromide is boiled with concentrated hydrochloric acid, it yields *hydroscopoline chloride hydrochloride*, $C_8H_{14}O_2NCl,HCl$, needles, m. p. 289° (decomp.). Many attempts have been made to oxidise this salt, in the hope of obtaining a chloroscopolic acid, but, almost always, the only product was found to be scopoline. With silver oxide and hot water, however, the strange result was the elimination of the *N*-methyl group, norscopoline being obtained.

A convenient method for the preparation of hydroscopoline is described. J. C. W.

The Linear Phenonaphthacridonequinone and Quinacridonequinone. W. St. Leśniański (*Ber.*, 1918, **51**, 695—706).—These compounds have been synthesised in order to determine whether quinones of the acridone series resemble anthraquinone derivatives in being vat dyes, which is found to be the case.

Anthranilic acid and α-naphthaquinone are heated together in alcoholic solution, when *o*-2-*naphthaquinonylaminobenzoic acid* (I) is formed. This crystallises in red needles, m. p. 271° (corr.), forms a dark red *silver* salt, and yields *phenonaphthacridonequinone* (II) on heating with concentrated sulphuric acid at 140—150°.

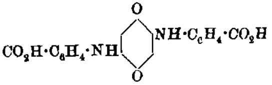
$$C_6H_4<\begin{matrix}CO-C\cdot NH\cdot C_6H_4\cdot CO_2H \\ \| \\ CO-CH\end{matrix} \qquad C_6H_4<\begin{matrix}CO\cdot C\cdot NH \\ \| \\ CO\cdot C-CO\end{matrix}>C_6H_4.$$

(I.) (II.)

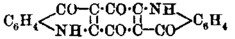
The quinone sublimes in orange needles, m. p. 384°, forms a red *potassium* salt, $C_{17}H_8O_3NK,H_2O$, and gives compounds with various acids, of which the *nitrate*, $B,2HNO_3$, pale yellow needles, is an example. On distillation with zinc dust, it yields dihydrophenonaphthacridine, m. p. 285—286° (Schöpff, A., 1895, i, 107), whilst reduction with sodium hyposulphite gives *dihydrophenonaphthacridonequinone* as a reddish-violet powder, m. p. 317° (corr.), which forms blue solutions in alkali hydroxides, from which cotton is dyed orange-yellow, and yields an orange *acetyl* derivative, m. p. 292° (corr.). *Dinitrophenonaphthacridonequinone*, a yellow powder, m. p. 299° (corr.), is obtained by the action of a warm mixture of fuming nitric and sulphuric acids.

The other quinone is obtained by heating benzoquinonedi-

anthranilic acid (III) (Ville and Astre, A., 1895, i, 465) with sulphuric acid at 145—155°. *Quinacridonequinone* (IV) is an

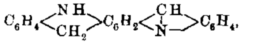


(III.)



(IV.)

amorphous, yellow powder, which partly sublimes and decomposes, without melting, at above 530°, and is insoluble even in solvents of high b. p. It forms a red, crystalline, *potassium* salt, $C_{20}H_9O_4N_2K,H_2O$, and an amorphous, brownish-yellow, *dipotassium* salt, $C_{20}H_8O_4N_2K_2,H_2O$, both of which are very easily hydrolysed, and it also yields an unstable *nitrate*, $B,4HNO_3$, long, golden-yellow needles, and a crystalline *sulphate*, $B,3H_2SO_4$. The quinone is practically indifferent to the action of alkalis, acylating, or ketone reagents, but yields *dihydroquinacridine*,



as a dark red. lustrous powder, m. p. 379° (corr.; decomp.), when distilled with zinc dust. It may also be reduced by means of sodium hyposulphite, but the bluish-violet product is insoluble. On warming with fuming nitric acid, it yields *dinitroquinacridonequinone*, $C_{20}H_8O_4N_2(NO_2)_2$, as a pale yellow, insoluble powder, which forms a dark red *potassium* salt, $2H_2O$. J. C. W.

Bromoalkylated Aromatic Amines. III. Derivatives of Ethylenediamine. J. VON BRAUN, K. HEIDER, and E. MÜLLER (*Ber.*, 1918, **51**, 737—741. Compare this vol., i, 107, 269).—The ω-bromoethyl derivatives of secondary amines react with other secondary bases to form compounds of the general formula $C_6H_5\cdot NR\cdot C_2H_4\cdot NR'R''$, where R′ and R″ may be both aliphatic radicles or one of them aromatic. The nitroso-derivatives of these may be deprived of the aromatic residues by hydrolysis, thus giving rise to alkylated ethylenediamines of the types

$$NHR\cdot C_2H_4\cdot NHR'$$

or $NHR\cdot C_2H_4\cdot NR'R''$, some of which are now described. The syntheses are comparatively simple and doubtless of manifold applicability.

s-Diphenyldimethylethylenediamine (*loc. cit.*, 108) gives a pale green *dinitroso*-compound, $C_2H_4(NMe\cdot C_6H_4\cdot NO)_2$, m. p. 208°, which forms an almost insoluble, greenish-brown *monohydrochloride*, m. p. 153°, and is hydrolysed by boiling with sodium hydrogen sulphite solution (D 1·21) to *s*-dimethylethylenediamine, m. p. 119° (Schneider, A., 1896, i, 200).

Methyl-β-bromoethylaniline (this vol., i, 108) reacts with ethylaniline or ethyl-β-bromoethylaniline (this vol., i, 270) with methylaniline to form *NN′-diphenyl-N-methyl-N′-ethylethylenediamine*, $NMePh\cdot C_2H_4\cdot NEtPh$, as a viscous liquid, b. p. 232—234°/21 mm.,

which gives a *picrate*, m. p. 176°, a pp′-*dibromo*-compound, needles, m. p. 100°, and a yellowish-green *dinitroso*-derivative, m. p. 190°. The latter is hydrolysed as above to s-*methylethylethylenediamine*, a mobile oil, b. p. 133°, which fumes in the air and forms a very hygroscopic *hydrochloride*,

$$NHMe{\cdot}C_2H_4{\cdot}NHEt,2HCl,$$

m. p. 217—218°, and a *platinichloride*, m. p. 240°.

Phenyltrimethylethylenediamine (this vol., i, 108) likewise gives rise to *trimethylethylenediamine*, $NHMe{\cdot}C_2H_4{\cdot}NMe_2$, which has b. p. 140° (about) and forms a very hygroscopic *hydrochloride*, m. p. 183°, a *platinichloride*, yellowish-red spikes from water, in which it is freely soluble, m. p. 230° (decomp.), and a *dipicrate*, m. p. 209—210°. J. C. W.

New Selenium Derivatives of Antipyrine. FRITZ VON KONEK and OSKAR SCHLEIFER (*Ber.*, 1918, **51**, 842—855).—The action of the selenium chlorides on antipyrine is described.

The monochloride reacts as though it were "selenoselenyl dichloride," $Se{:}SeCl_2$. When a solution in carbon tetrachloride is added to a concentrated solution of antipyrine in chloroform at 0°, *diantipyryl diselenide* (or *selenoselenide*),

$$Se{:}Se{:}\left[C{<}\begin{matrix}CMe{\cdot}NMe\\ CO{-}NPh\end{matrix}\right]_2,$$

is deposited. This crystallises from about 40% alcohol in yellow needles, m. p. 215—216°, and deposits elementary selenium when boiled with hydrochloric acid, the solution containing the salt of *diantipyryl selenide*. This compound is precipitated by the addition of sodium carbonate; it crystallises from benzene in pearly flakes, m. p. 240°, and forms a *dihydrochloride* and a *compound* with mercuric chloride. It may be identical with a substance mentioned in D.R.-P. 299510 (1917), obtained from antipyrine by the action of selenium dioxide and concentrated sulphuric acid.

Selenium tetrachloride also reacts vigorously, giving *diantipyrylselenium dichloride*, $(C_{11}H_{11}ON_2)_2SeCl_2$, which crystallises from benzene in pearly scales, m. p. 225°, and changes into the above selenide on treatment with alkalis.

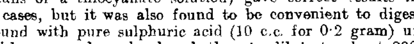
Some notes on the analysis of organo-selenium compounds are given in an appendix. For the estimation of carbon and hydrogen, the long combustion tube is filled with copper oxide and lead chromate in equal layers, with a layer of lead peroxide, about 12—15 cm. long, kept at 180—200°, in the front. The various methods for estimating selenium have been tested, but not one is found to be entirely satisfactory. Oxidation with nitric acid or nitric acid and potassium chlorate is accompanied by loss of selenium in the fumes; for the oxidation by sodium peroxide, a large excess of the reagent must be used, otherwise some free selenium will be obtained, and the quantitative reduction of the sodium selenate formed to the element cannot be achieved; combustion in oxygen in a bomb sometimes results in loss by the

alloying of selenium with the platinum wires and also the production of oxides other than the desired selenic oxide (see this vol., ii, 309). Frerich's method (decomposition with fuming nitric acid in the presence of silver nitrate, evaporation, filtration of the silver selenite, and titration of this in dilute nitric acid solution by means of a thiocyanate solution) gave correct results in the above cases, but it was also found to be convenient to digest the compound with pure sulphuric acid (10 c.c. for 0·2 gram) until a brownish-green colour developed, then to dilute to about 200 c.c., saturate with sulphur dioxide, leave overnight, and collect the precipitate of selenium. The drawback to this method is that it is difficult to tell just when to stop the action of the sulphuric acid, as it must not proceed to the production of much selenious acid.

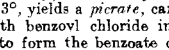
J. C. W.

Synthesis of some New Naphthylpyrazolones. Fritz von Konek and Richard Mitterhauser (*Ber.*, 1918, **51**, 865—871).—The application of some naphthylhydrazines in the synthesis of pyrazolones is described.

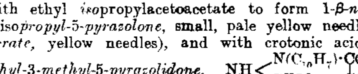
β-Naphthylhydrazine and ethyl benzylacetoacetate produce 1-*β-naphthyl-4-benzyl-3-methyl-5-pyrazolone* (I), which crystallises in rosettes of pale pink needles, m. p. 153°, yields a *picrate*, canary-yellow, matted needles, and reacts with benzoyl chloride in the presence of sodium hydroxide solution to form the benzoate of its enolic modification, namely, 5-*benzoyloxy*-1-*β-naphthyl-4-benzyl-3-methylpyrazole* (II), yellow needles, m. p. 138°. The same base



(I.) (II.)

reacts with ethyl *iso*propylacetoacetate to form 1-*β-naphthyl-3-methyl-4-*iso*propyl-5-pyrazolone*, small, pale yellow needles, m. p. 160° (*picrate*, yellow needles), and with crotonic acid to give 1-*β-naphthyl-3-methyl-5-pyrazolidone*, , pale brown crystals, m. p. 107°. Aceto-β-naphthylhydrazide (from the base and acetamide) reacts with ethyl benzylacetoacetate and phosphorus trichloride to form 1-*β-naphthyl-4-benzyl-5-methyl-3-pyrazolone*, yellow needles, m. p. 208°.

α-Naphthylhydrazine gives rise to 1-*α-naphthyl-4-benzyl-3-methyl-5-pyrazolone*, pale yellow rosettes, m. p. 168°, which forms a yellow *picrate* and reacts with nitrous acid to yield a *bis-pyrazolone*,



brown crystals, m. p. 215°.

pp'-Dihydrazinodiphenyl and ethyl benzylacetoacetate condense at 160° to form 4 : 4'-*diphenylenebis-4-benzyl-3-methyl-5-pyrazolone*, $C_{34}H_{30}O_2N_4$, as a yellow powder.

J. C. W.

Synthesis of Iminouracil-6-acetic Acid. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1918, **40**, 1133—1135).—Guanidine carbonate and ethyl acetonedicarboxylate readily condense in boiling alcoholic solution to give a 90% yield of *guanidine 2-iminouracil-6-acetate*, $NH<\begin{matrix}CO\text{———}CH\\C(:NH)\cdot NH\end{matrix}>C\cdot CH_2\cdot CO_2H,CH_5N_3$, microscopic needles, decomp. 213—214° with formation of an amorphous solid, m. p. 230°. A solution of the salt forms with a solution of copper sulphate dark green, diamond-shaped crystals. *2-Iminouracil-6-acetic acid,* liberated from the guanidine salt by hydrochloric acid, crystallises from water in colourless, square plates, m. p. 289—290° (decomp.), decomposes soluble carbonates, reacts with bromine to form a *substance*, needles, m. p. 210—211° (decomp.), and with concentrated nitric acid at 70° to form an amorphous, yellow *5-nitro*-derivative, decomp. 309—310°. The sodium salt and copper sulphate solution yield a light green precipitate consisting of microscopic, pointed, twinned plates intersecting at right angles.

C. S.

Hydrogen Peroxide as a Reagent in the Purine Group. II. Action of Hydrogen Peroxide on Uric Acid. C. S. VENABLE (*J. Amer. Chem. Soc.*, 1918, **40**, 1099—1120. Compare Venable and Moore, this vol., i, 104).—The usual course of the experiments is to treat an aqueous solution of uric acid with a definite volume of $6N$-sodium hydroxide, to bring the mixture to the desired temperature, and to add the hydrogen peroxide, usually in 3% solution. At definite intervals, samples are taken and analysed. The temperature range is 20—90°, and the excess alkali concentration from 0 to $0{\cdot}5N$. Three different products are formed, according to the experimental conditions. In weakly alkaline or neutral solutions and at temperatures near that of boiling water, allantoin is first formed in large quantities, together with smaller amounts of carbonyldicarbamide, but no genetic relationships connecting the two substances have been discovered; they appear to be products of two independent reactions. As the oxidation proceeds, the amount of carbonyldicarbamide remains fairly constant, but the yield of allantoin rapidly diminishes, with the appearance of increasing amounts of cyanuric acid up to a maximum yield of 10%. Increasing the alkalinity at this high temperature rapidly diminishes the yield of all three substances, until with an excess alkalinity of $0{\cdot}1N$ only very small amounts of cyanuric acid are obtained. At lower temperatures and in weakly alkaline solutions the same phenomena were observed, the disappearance of the allantoin being much slower. On increasing the alkalinity, the yield of cyanuric acid rapidly increased, with a corresponding decrease in the yields of both allantoin and carbonyldicarbamide. At 20° and with an excess alkalinity of $0{\cdot}5N$, no allantoin or carbonyldicarbamide was observed, whilst the yield of cyanuric acid was as high as 50% of the theoretical. Further increase of alkalinity or lowering of the temperature was apparently without effect. The

preceding high yield of cyanuric acid required explanation, because it was found that under the experimental conditions allantoin was rapidly decomposed by hydrogen peroxide without producing cyanuric acid, and the largest yield of carbonyldicarbamide was 15%, which, assuming a quantitative conversion to cyanuric acid and adding the 10% of the latter already present, only accounts for a 30% yield of cyanuric acid. Furthermore, the conversion of 1 mol. of carbonyldicarbamide to 1 mol. of cyanuric acid requires the liberation of 1 mol. of ammonia, whereas the molecular ratio of ammonia formed to cyanuric acid recovered was found to be less than 1:3. Also, in all oxidations at low temperature and high excess of alkali, no allantoin or carbonyldicarbamide was obtained throughout the course of the oxidation (twenty-four hours), and carbonyldicarbamide, oxidised under similar conditions, was not entirely converted into cyanuric acid even after forty-eight hours. These facts indicate that the oxidation of uric acid by hydrogen peroxide at low temperatures and high excess of alkali is fundamentally different from that occurring at high temperatures and a low concentration of alkali, and that some intermediate product must exist in the alkaline solution after oxidation, which is decomposed during the acidification, constituting the first step in the analysis of the products. To test this point, the alkaline solution resulting from the oxidation was treated with manganese dioxide to destroy the excess of hydrogen peroxide, and was then neutralised by acetic acid, whereby a 60% yield of a mixture of the normal and the acid salts of a dibasic *acid*, $C_4H_5O_5N_3$ [*ammonium* salt, $C_4H_3O_5N_3(NH_4)_2$], was obtained. This acid, oxidised in acid solution by hydrogen peroxide, gives an 80% yield of cyanuric acid; it cannot be converted into allantoin, carbonyldicarbamide, or uroxanic acid (see also next abstract).

The formation of cyanuric acid is in all cases a secondary reaction. It may be formed by the alkaline oxidation of allantoin, especially in neutral solution at high temperature, by the action of alkali alone on carbonyldicarbamide, and, in the best yield, from the acid, $C_4H_5O_5N_3$, as above.

Attempts to trace a parallelism between the oxidising action of hydrogen peroxide and of potassium permanganate on uric acid have been unsuccessful. C. S.

Hydrogen Peroxide as a Reagent in the Purine Group. III. Allantoxanic Acid as an Oxidation Product of Uric Acid. F. J. Moore and Ruth M. Thomas (*J. Amer. Chem. Soc.*, 1918, **40**, 1120—1132. Compare preceding abstract).—The best conditions for preparing Venable's acid, $C_4H_5O_5N_3$, are the oxidation by hydrogen peroxide at the ordinary temperature of an alkaline solution of uric acid, the excess alkalinity of which is approximately normal. The ammonium salt when heated in a sealed tube at 150° is converted almost quantitatively into ammonium carbonate and allantoxaidine, the latter also being formed when the barium salt is treated with a slight excess of

sulphuric acid and the filtrate is evaporated. This suggests that Venable's acid is hydrated allantoxanic acid, $C_4H_3O_4N_3,H_2O$, and the suggestion is confirmed by the identity of its ammonium salt with ammonium allantoxanate prepared by Ponomarev's method and by its reduction to hydroxonic (dihydroallantoxanic) acid by sodium amalgam.

In the formation of allantoxanic acid from uric acid by hydrogen peroxide, neither allantoin nor glycol-uril is an intermediate product. The oxidation of allantoxanic acid to cyanuric acid by hydrogen peroxide in acid solution does not pass through allantoxaidine. C. S.

Acetyl-*p*-diazoimides Derived from Substituted *p*-Phenylenediamines. GILBERT T. MORGAN and DAVID ALEXANDER CLEAGE (T., 1918, **113**, 588—596).—The general nature of the reaction by which acyl-*p*-diamines can be converted into acyl-*p*-diazoimides, although indicating the considerable influence of the acyl group on the intramolecular condensation, nevertheless does not preclude the possibility of isolating the parent substances of this series of diazo-compounds. Derivatives of *p*-phenylenediamine containing acidic substituents in the nucleus have therefore been submitted to examination.

2-Nitro-*p*-phenylenediamine in dry acetone reacts with nitrous anhydride, yielding *3-nitro-*p*-phenylene-1-diazo-4-imide,*

$$NH{:}C\begin{matrix}<C(NO_2){:}CH>\\<CH{=}{=}CH>\end{matrix}C<\begin{matrix}N\\ \|\\ N\end{matrix},$$

a brown, crystalline solid which becomes resinous when warmed to the ordinary temperature. The *acetyl* derivative of this substance, brownish-red plates, which explode at 140°, combines with *β*-naphthol, with formation of *3-nitro-4-acetylaminobenzeneazo-β-naphthol*, $NHAc{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$, a dark red powder, m. p. above 290°; this substance on hydrolysis gives *3-nitro-4-aminobenzeneazo-β-naphthol*, a pale brown powder, m. p. 208°, which after further diazotisation reacts with *β*-naphthol, producing a *bisazo*-derivative, and with hot alcohol producing *3-nitrobenzeneazo-β-naphthol*, orange crystals, m. p. 192°. The identity of the last substance, which serves to confirm the constitution ascribed to the above nitroacetylphenylenediazoimide, is demonstrated by direct comparison with a specimen synthesised from *m*-nitroaniline. Further evidence as to the constitution is adduced by the preparation of the isomeric *2-nitro-4-acetyl-*p*-phenylene-1-diazo-4-imide*, $C_8H_6O_3N_4$, decomp. 142° (with explosion), by the interaction of 2-nitro-4-acetyl-*p*-phenylenediamine and nitrous anhydride in dry acetone; this combines with *β*-naphthol, giving rise to *2-nitro-4-acetylaminobenzeneazo-β-naphthol*, a red substance, m. p. 298°, the hydrolysis of which yields *2-nitro-4-aminobenzeneazo-β-naphthol*. By further diazotisation, this product can be made to combine again with *β*-naphthol, giving a bisazo-compound, and also to undergo reduction by hot alcohol to 2-nitrobenzeneazo-*β*-naphthol, the

identity of which is also confirmed by direct comparison with a specimen prepared from *o*-nitroaniline.

In a similar manner, 2 : 6-dichloro-*p*-phenylenediamine is found to react with nitrous anhydride in dry acetone, giving unstable 3 : 5-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide*, which yields a more stable 4-*acetyl* derivative, a grey, crystalline powder, decomp. 138° with explosion. This acetyl derivative gives colour reactions with the naphthols and naphthylamines identical with those exhibited by the yellow 3 : 5-dichloro-4-acetyl-*p*-phenylene-1-diazo-4-imide, decomp. at 133°, obtained by diazotising 2 : 6-dichloro-1-acetyl-*p*-phenylenediamine, and the suggestion is made that the almost colourless and yellow forms of the acetyl compound may be represented by the cyclic diazoimide constitution, $C_6H_2Cl_2{<}\genfrac{}{}{0pt}{}{NAc}{N_2}$, and the diazoquinoneimide constitution, $NAc{:}C_6H_2Cl_2{<}\genfrac{}{}{0pt}{}{N}{N}$ respectively, the difference disappearing on combination with phenols or bases. 2 : 6-*Dichloro-4-acetyl*-p-*phenylene*-1-*diazo-4-imide*, $C_8H_5ON_3Cl_2$, almost colourless plates, decomp. at 138°, obtained from 2 : 6-dichloro-4-acetyl-*p*-phenylenediamine, is to be regarded as probably of cyclic diazoimide structure. D. F. T.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. F. Knoop (*Zeitsch. physiol. Chem.*, 1918, **101**, 210—211. Compare Mörner, this vol., i, 198).—The unidentified acid substances discovered by Mörner (*loc. cit.*) amongst the oxidation products of protein are probably 5-nitroglyoxaline-4-carboxylic acid, $C_4H_3O_4N_3$ (Windaus and Opitz, A., 1911, i, 752), and glyoxaline-4-glyoxylic acid, $C_5H_4O_3N_2$ (Knoop, A., 1907, i, 788). Both substances are oxidation derivatives of histidine and have the properties described by Mörner. Attention is directed to the fact that the latter substance, $C_5H_4O_3N_2$, must contain either 2 or 4 atoms of hydrogen instead of 3 (as found by Mörner) if it consists of a simple molecule. H. W. B.

Preparation of Ovalbumin, and its Refractive Indices in Solution. A. R. C. Haas (*J. Biol. Chem.*, 1918, **35**, 119—125).—The crystallisation of ovalbumin is found to be dependent on the hydrogen ion concentration of the globulin-free solution of white of egg; crystals are formed in the presence of ammonium sulphate when the hydrogen ion concentration lies between 10^{-5} and 10^{-6}.

The refractive indices of solutions of ovalbumin in water, 1% ammonium sulphate, and in various concentrations of sodium hydroxide obey the law $n - n_1 = a \times c$, where n is the observed refractive index of the protein solution, n_1 that of the solvent, c the percentage of dissolved protein, and a a constant, which is found to be 0.00177 ± 0.00006. The corresponding constant for the albumins of ox serum is 0.00177 ± 0.00008 (Robertson, A., 1912, ii, 611). H. W. B.

Preparation of Pure Caseinogen. Lucius L. Van Slyke and John C. Baker (*J. Biol. Chem.*, 1918, **35**, 127—136).—The caseinogen is prepared from undiluted milk by treatment with normal acid, preferably lactic or a mixture of 1 part of hydrochloric and 2 parts of acetic acid. The acid is introduced slowly into the milk below the surface, the tip of the tube carrying the acid being so arranged that it is very close to a mechanical stirrer revolving at a high speed and also near the bottom of the vessel containing the milk. Under these conditions, the acid does not cause coagulation of the caseinogen at the point where the acid first comes into contact with the milk.

The product, the preparation of which requires only about ten hours, is a fine, white powder containing 0·10% of ash and 0·80% of phosphorus. It is free from inorganic phosphorus, calcium, and hydrolytic products of protein, and dissolves at once in dilute solutions of monoacidic alkalis to a clear solution. H. W. B.

Constitution of the True Nucleic Acids. R. Feulgen (*Zeitsch. physiol. Chem.*, 1918, **101**, 288—295. Compare this vol., i, 85, and Levene and Jacobs, A., 1912, i, 926).—A theoretical paper in which the general arrangement of the nucleotides in nucleic acid suggested by Levene is accepted, although the precise method of linking together of the nucleotides is regarded as unsettled (compare also Jones and Read, A., 1917, i, 232, 233).

H. W. B.

Preparation and Properties of Thymic Acid. R. Feulgen (*Zeitsch. physiol. Chem.*, 1918, **101**, 296—309).—Thymic acid is prepared by treating sodium nucleinate with a slight excess of sulphuric acid and keeping the mixture for forty minutes at 80°. The acid is separated in the form of its barium salt, and on hydrolysis yields cytosine and thymine. H. W. B.

Influence of Normal Salts, Bases, and Acids on the Precipitability of Gelatin by Alcohol. Jacques Loeb (*J. Biol. Chem.*, 1918, **34**, 489—501. Compare this vol., i, 240).—In these experiments, finely powdered gelatin is treated for an hour with solutions of normal salts, bases, or acids of various concentrations; the excess of the solution is in each case washed away with water, a 1% solution of the washed gelatin in water being then prepared and treated with alcohol until precipitation just occurs. It is found that when the concentration of the salt solution exceeds a certain limit, which is about $M/128$ in the case of normal salts with univalent anions and cations and monoacidic bases, the gelatin becomes non-precipitable by alcohol, whilst in the case of normal salts with bivalent anion and univalent cation, and also in the case of strong monobasic acids, the concentration at which non-precipitability occurs is just twice as great, namely, $M/256$. After treatment with solutions of normal salts with bivalent cations and univalent or bivalent anions, the gelatin remains precipitable

with alcohol for all the concentrations of the salt used. These experiments confirm the conclusions previously drawn by the author in former papers (*loc. cit.*). H. W. B.

Action of Pancreatic Enzymes on Casein. H. C. SHERMAN and DORA E. NEUN (*J. Amer. Chem. Soc.*, 1918, **40**, 1138—1145).—A comparative study of the hydrolysis of casein by various preparations derived from the pancreas. Extraction of high-grade commercial pancreatin with 50% alcohol leaves a residue having about the same proteolytic activity as the original pancreatin. The "sac precipitate" which settles out of the amylase solution during the dialysis in 50% alcohol preceding the final precipitation of the amylase preparation (Sherman and Schlesinger, A., 1912, i, 815; 1915, i, 604) has fifteen times the proteolytic activity of the original pancreatin and about four times that of the most active commercial trypsin. The final preparation of pancreatic amylase, purified as described previously (*loc. cit.*), has proteolytic activity fully as great as that of high-grade trypsin. C. S.

Enzyme Chemistry. H. VON EULER (*Zeitsch. Elektrochem.*, 1918, **24**, 173—177).—In the inversion of sucrose by yeast, it is shown that the invertase increases to a maximum and the formation of the enzyme follows the formula $dx/dt=k(a-x)$. Other experiments on the hydrolysis of starch by the enzyme of *Mucor mucedo* are described, in this case, the velocity of the formation of the enzyme is constant. J. F. S.

The Law of Action of Sucrase. H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1918, **167**, 208—210).—The inversion of sucrose by sucrase does not obey Wilhelmy's law, $x=a(1-e^{-kt})$, at concentrations of sucrose exceeding 2% or 3%, but there is probably a definite ratio of sucrose to sucrase below which the law holds good. Using 5 c.c. of a very active sucrase preparation, the authors have obtained results in agreement with the law up to concentrations of 2% of sucrose. W. G.

Chemical Reaction in the System: Urea-Urease. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1918, **39**, 125—184).—Ammonium carbamate has always been found by Fenton's method in the product of the action of urease on urea. It may therefore be presumed that the decomposing action of urease is a successive hydrolysis of urea, $NH_2{\cdot}CO{\cdot}NH_2 \longrightarrow NH_2{\cdot}CO_2{\cdot}NH_4 \longrightarrow (NH_4)_2CO_3$, in opposition to the view of the formation of an intermediate product of urea and urease.

The experiments were always carried out in a slightly acidic solution obtained by saturating the reacting system with carbon dioxide. Notwithstanding the phase difference of the two constituents of the reaction, it seems to be a homogeneous chemical reaction, because stirring has no effect on its velocity. The velocity constant k_1 of the first hydrolysis was determined by the initial

velocity, and the constant k_2 of the second hydrolysis by some trials. With a 0·02*N*-solution of urea and a solution of urease containing 0·2 gram in 100 c.c., the values obtained were $k_1=0·0068$, $k_2=0·00617$ at 25°. These constants vary proportionately to the concentration of the urease. A good coincidence was obtained between the observed values for the velocity of the reaction and the values for k_1 and k_2 calculated by the formula derived from Rakowski's general theory of unimolecular successive chemical reactions (A., 1907, ii, 74). The temperature coefficient of this reaction is 2 per 10° between 15° and 35°. Many reagents are adsorbed by urease and show a poisonous action; the action of alkali hydroxide is reversible, whilst that with hydrochloric acid, mercuric chloride, or silver sulphate is irreversible. S. H.

Synthesis of Organic Sodium Derivatives. ANTONIO MADINAVEITIA and JOSÉ RANEDO (*Anal. Fis. Quim.*, 1918, **16**, 142—145).—Dimethylaniline reacts with mercuric acetate to form dimethylaniline mercury acetate, $Me_2N·C_6H_4·Hg·CO_2Me$, which is transformed by sodium hyposulphite into mercury *pp*-tetramethyldiaminodiphenyl, $(Me_2N·C_6H_4)_2Hg$. The solution of this substance in benzene reacts with sodium, the mercury being replaced by the alkali metal. The mechanism of the process is similar to the formation of sodium phenyl by the interaction of sodium and mercury phenyl. The sodium compound is spontaneously inflammable on contact with air. A. J. W.

Simplified Method for the Preparation of Tin Triaryl Haloids. ERICH KRAUSE (*Ber.*, 1918, **51**, 912—914).—If the tin tetra-aryls are brominated in ordinary organic media, or alone, no matter how carefully the conditions are controlled, the main products are the tin diaryl dibromides. If the compounds are suspended in pyridine chilled by means of solid carbon dioxide, however, bromination can be stopped at the first stage. The product is freed from solvent and bromobenzene (or analogous compound) by distillation, then transferred to ether, and shaken with 30% sodium hydroxide. The *tin triaryl hydroxide* dissolves in ether, and can be converted into any desired haloid by means of the acids.

Tin triphenyl chloride, $SnPh_3Cl$, m. p. 106°, b. p. 240°/13·5 mm. (compare Aronheim, A., 1879, 250, 651), *bromide*, fern-like groups of octahedra, m. p. 120·5°, b. p. 249°/13·5 mm., and *iodide*, large, snow-white, quadratic, monoclinic prisms, m. p. 121°, b. p. 253°/13·5 mm., have been prepared in this way in yields amonnting to 90—95%. J. C. W.

Physiological Chemistry.

Comparative Study of the Influence of Carbohydrates and Fats on the Nutritive Power of Alimentary Proteins. F. Maignon (*Compt. rend.*, 1918, **167**, 172—175. Compare this vol., i, 359).—Feeding experiments with rats, using diets of egg-albumin and fat, or egg-albumin and starch, or a mixture of the three, indicate that the albumin is better utilised with the fat than with starch, and that the minimum of albumin necessary is much lower with fat than with starch. The most satisfactory mixture of albumin and fat is in the proportion 1 : 1, even if starch is present.
W. G.

The Nutritive Equilibrium of the Animal Organism. Jules Amar (*Compt. rend.*, 1918, **167**, 241—242).—The author points out that Maignon's results for fat and starch as supplements to protein in feeding rats (compare preceding abstract) are in opposition to those of Atwater and Benedict (compare A., 1903, ii, 308) and Mendel and Lewis (A., 1913, i, 1406). He directs attention to his own work in this connexion (compare *Moteur humain*, 1909, 289).
W. G.

Nitrogenous Metabolism of the Central Nervous System. Else Hirschberg and Hans Winterstein (*Zeitsch. physiol. Chem.*, 1918, **101**, 212—222. Compare this vol., i, 52).—The isolated spinal cord of the frog contains in the fresh material 1·30% of nitrogen, and 1·25% in cords freed from the outer membranes. The content of nitrogen is unaltered by preservation of the cords in air or oxygen, but falls rapidly when immersed in oxygenated saline solution. The addition of a trace of a calcium salt to the saline solution increases the rate of loss of nitrogen from the cord; potassium salts decrease it. Treatment with 4% of alcohol practically arrests nitrogenous metabolism; electrical stimulation increases it nearly fourfold. The katabolic action is an oxidative one, because it fails to occur in the absence of free oxygen.
H. W. B.

Utilisation of various Saccharides in the Metabolism of the Central Nervous System. Else Hirschberg (*Zeitsch. physiol. Chem.*, 1918, **101**, 248—254. Compare Hirschberg and Winterstein, this vol., i, 52).—Maltose and sucrose are not utilisable for the maintenance of the metabolic processes of the surviving spinal cords of frogs. Dextrose and lævulose have about equal power in maintaining metabolism in the resting state, whilst lactose has less and galactose considerably more, probably due to the participation of the latter substance in the composition of nervous tissue. During excitation, the consumption of dextrose by the tissue greatly exceeds that of any other saccharide other than

galactose. Dextrose is therefore the best material to supply for the rapid production of power for the use of nervous tissues.

H. W. B.

Oxidation Catalysts in the Animal Organism. Action of certain Ferments on Oxydones. LEOPOLDO LÓPEZ PÉREZ (*Anal. Fís. Quím.*, 1918, **16**, 397—421).—A full account of work of which a preliminary note has appeared (see this vol., i, 88).

Origin of Creatine. III. L. BAUMANN and H. M. HINES (*J. Biol. Chem.*, 1918, **35**, 75—82).—Perfusion of dog muscle with choline or sarcosine leads apparently to the production of creatine. Arginine, histidine, betaine, methylguanidine, and cyanamide when similarly treated do not yield any notable increase in the amount of creatine in muscle or urine. H. W. B.

Amino-acids of Mature Human Placenta. VICTOR JOHN HARDING and CHARLES ATHERTON FORT (*J. Biol. Chem.*, 1918, **35**, 29—41).—The amount of arginine in human placenta is twice as much as that present in any other human organ (liver, heart, kidney, muscle). H. W. B.

Caseinogen of Human Milk. A. W. BOSWORTH and LOUISE A. GIBLIN (*J. Biol. Chem.*, 1918, **35**, 115—117).—Caseinogen prepared from human milk resembles the caseinogen prepared from cows' and goats' milk in the following respects: It has the same nitrogen, phosphorus, and sulphur content, the same molecular weight and degree of valency; it gives the same series of salts with bases; it is acted on by rennin in the same manner, producing the same casein. H. W. B.

Free Lactic Acid in Sour Milk. LUCIUS L. VAN SLYKE and JOHN C. BAKER (*J. Biol. Chem.*, 1918, **35**, 147—178).—Lactic acid exists in sour milk largely as lactate, but partly as free acid, some of the latter being in solution, whilst a smaller part is adsorbed by the caseinogen or casein. Sterilised milk inoculated with *Bacterium lactis acidi* does not show the presence of free lactic acid until about twenty hours after the inoculation; the amount then rapidly increases and reaches about 20 c.c. of $0 \cdot 1N$-acid in forty-eight hours. The p_H value changes from 6·5 in fresh milk to 4·17 in forty-eight hours. The caseinogen begins to coagulate when the p_H reaches 4·64 to 4·78. During the coagulation process, the hydrogen-ion concentration remains constant, although the acidity by titration increases slightly. About 20% of the free lactic acid in coagulated sour milk is adsorbed by the casein.

The first perceptible sign of souring in milk is a characteristic flavour, discernible to the senses of both taste and smell, due to the presence of a volatile compound formed in the souring process, and not to lactic acid. There does not appear to be any relation between either hydrogen-ion concentration or acidity by titration and the first sign of this flavour.

Various methods are described for estimating the free lactic acid and of that portion of it which is adsorbed by the caseinogen or casein. H. W. B.

Glycerides of Butter Fat. CONRAD AMBERGER (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 313—381).—Butter fat contains only a small quantity (2·4%) of triolein, the greater part of the oleic acid existing in the fat in the form of mixed glycerides. If the oleic acid is present as triolein, the fat when hydrogenised should yield a corresponding quantity of tristearin, but such is not found to be the case. Butyric and other volatile acids are also present in the fat as mixed glycerides; tributyrin cannot be isolated. Examination of the alcohol-soluble portion of hydrogenised butter fat shows that the original fat contains butyrodiolein, butyropalmito-olein, and oleodipalmitin. The author has also isolated from butter fat a glyceride, m. p. 67·9°, and yielding mixed fatty acids, m. p. 55·5°. W. P. S.

Transformation of Tetrahydronaphthalene (Tetralin) in the Animal Body. G. SCHROETER and K. THOMAS (*Zeitsch. physiol. Chem.*, 1918, **101**, 262—275).—Tetrahydronaphthalene fed to a dog is absorbed and eventually excreted in combination with urea. The existence of four compounds of tetrahydronaphthalene and carbamide is theoretically possible, and the authors have succeeded in preparing all of them by the interaction of potassium cyanate on the respective amines in aqueous solution. ar-*Tetrahydro-α-carbamidonaphthalene*, $C_{11}H_{14}ON_2$, crystallises in square plates from alcohol, softens at 198°, and melts at about 206° (quickly heated, at 212°); ar-*tetrahydro-β-carbamidonaphthalene*, needles from water, m. p. 134° (decomp.); ac-*tetrahydro-α-carbamidonaphthalene*, needles, m. p. 210·5°; ac-*tetrahydro-β-carbamidonaphthalene*, needles, m. p. 183°. Comparison of the natural product with these compounds shows that tetralin in its passage through the body is converted into *dl-ac*-tetrahydro-α-carbamidonaphthalene.

In the preparation of the *ar*-β-compound, a small amount of a substance was obtained in the form of colourless needles, which did not melt below 245° and possessed the composition of *di*-ar-*tetrahydro-β-naphthylcarbamide*, $(C_{10}H_{12}N)_2CO$. H. W. B.

Relation between the Chemical Structure of the Opium Alkaloids and their Physiological Action on Smooth Muscle with a Pharmacological and Therapeutic Study of some Benzyl Esters. I. Relation of the Chemical Structure of the Opium Alkaloids to their Action on Smooth Muscle. DAVID I. MACHT (*J. Pharm. Expt. Ther.*, 1918, **11**, 389—417).—The results indicate that in respect to their physiological action on the rhythmic contraction and tonicity of smooth muscle from various organs, the opium alkaloids can be divided into two classes: (1) the morphine group; (2) the papaverine group. Members of

the first group, containing a pyridine–phenanthrene nucleus, exert a stimulating action which appears to be associated with the pyridine or piperidine component of the molecule, whilst the members of the papaverine or benzyl*iso*quinoline group exert an inhibitory action which can be traced to the benzyl radicle. Alkaloids such as benzylmorphine or peronine, containing both significant groupings, have an anomalous action on smooth muscle.
H. W. B.

Pharmacology of the Vitamines. FR. UHLMANN (*Zeitsch. Biol.*, 1918, **68**, 419—456).—The administration of vitamines to cats and dogs, either subcutaneously, intravenously, or by the mouth, causes a marked stimulation of the salivary, sweat, gastric, and other glands which is inhibited by atropine. The author considers that the vitamines in the food play an essential part in the processes of digestion and metabolism through their stimulatory action on glands producing external and internal secretions. The commercial vitamine preparation "orypan," obtained from rice husks, was chiefly employed, but similar results were given in some experiments by extracts of oats, meat, yeast, etc. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Occurrence of Methylpentosans in Cereals and Legumes. KINTARÔ ÔSHIMA and KINSUKE KONDÔ (*J. Tokyo Chem. Soc.*, 1918, **39**, 294—300).—On account of incompleteness of the method of determination of methylpentosans, there has been doubt as to their occurrence in some seeds in which they have been reported to exist. The authors have therefore examined certain cereals and legumes by their improved method (this vol., ii, 338), and have found methylpentosans in all varieties of the soja bean, whilst it is absent in the cereals investigated. S. H.

Phytochemistry of the Crowberry (Empetrum nigrum). L. VAN ITALLIE (*Pharm. Weekblad*, 1918, **55**, 709—717).—The leaves of *Empetrum nigrum* contain a wax composed wholly, or in great measure, of ceryl cerotate, benzoic acid, urson, tannin, dextrose, and probably rutin. The anhydrous urson has the formula $C_{10}H_{16}O$, and is identical with the derivative obtained from the leaves of *Uva Ursi*.

Empetrum nigrum contains no alkaloids, andromedotoxins, or glucosides decomposed by emulsin. The presence of benzoic acid and urson points to a probable relationship between the *Empetraceæ* and *Eriaceæ*. A. J. W.

Plant Sterols. I. Sterol Content of Wheat (Triticum sativum). MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 160—172). —*The chief phytosterol present in the wheat grain is sitosterol.* The embryo also contains sitosterol, but the phytosterol in the bran differs in its properties from sitosterol. The unsaponifiable ether extract of the vegetative organs, leaves, stems, etc., contains a phytosterol, together with an *alcohol*, $C_{20}H_{42}O$, crystallising from ethyl acetate and acetone in granular lumps of small crystals, m. p. 83°; *acetate*, m. p. 65°; it does not give the cholesterol colour reactions.

The amount of phytosterol in normal wheat plants is greater *than that which was present in the grain from which the plants* were grown; in etiolated plants, an increase in the phytosterol content as compared with the grain is not perceptible. It is suggested that the sterols form an essential part of cell membranes.

H. W. B.

Plant Sterols. II. Occurrence of Phytosterol in some of the Lower Plants. MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 173—177).—Ergosterol and fungisterol occur in the fungus *Polyporus nigricans*, and probably also in *P. betulinus*. Sterols may also be detected in *Laminaria*, *Sphagnum*, *Agaricus rubescens*, and *Lactarius subdulcis*. H. W. B.

Some Poisonous Plants in the Order Solanaceæ. II. Nicotiana suaveolens. J. M. PETRIE (*Proc. Linn. Soc. N.S. Wales*, 1916, **41**, 148—151; from *Physiol. Abstr.*, 1918, **3**, 199).—This plant contains nicotine. S. B. S.

The Production of Anthocyanins and Anthocyanidins. III. ARTHUR ERNEST EVEREST (*Proc. Roy. Soc.*, [*B*], **90**, 251—265. Compare A., 1914, i, 978; 1915, i, 25).—The author has isolated the anthocyanin pigment from the purplish-black viola, "Black Knight," petals, and has shown that it is a delphinidin glucoside and identical with the violanin obtained by Willstätter and Weil from the bluish-black pansy (compare *Annalen*, 1916, **412**, 178). An examination of the alum reaction as described by Willstätter and his collaborators shows that the colour reactions of anthocyanins, described as due to alum, are really due to the presence of iron as an impurity in the alum, and are not obtained if the reagent is pure.

An examination of the yellow sap pigment from the same violas shows that it contains a myricetin glucoside (or less probably a gossypetin glucoside) and also another yellow sap pigment which does not give a green coloration with dilute alkalis. Thus the presence in one flower of an anthocyanin pigment and of the flavonol derivatives from which it would be produced by reduction is shown for the first time. W. G.

Organic Chemistry.

Synthesis of $\alpha\delta\eta$-Heptanetriol, True Homologue of Ordinary Glycerol, and of some Derivatives of Propyltetrahydrofuran. J. Hamonet (*Ann. Chim.*, 1918, [ix], **10**, 5—30).—In part a more detailed account of work already published (compare A., 1916, i, 246). When $\alpha\eta$-dimethoxyheptan-δ-ol is acted on by phosphorus tri-iodide, it yields methyl iodide and 2-γ-*methoxypropyltetrahydrofuran*, b. p. 190—192°, D^{18} 0·9559, n_D^{15} 1·440, and not the required iododimethoxyheptane. Similar attempts to prepare the corresponding bromo-compound were not successful, but δ-*chloro-$\alpha\eta$-dimethoxyheptane*, b. p. 120—122°/16 mm., was obtained by the action of phosphorus trichloride. $\alpha\eta$-Dibromoheptan-δ-ol (*loc. cit.*), when distilled, decomposed, giving 2-γ-*bromopropyltetrahydrofuran*, b. p. 115—116°/27 mm., D^{20} 1·331, n_D^{20} 1·485. W. G.

Preparation of certain Alkylating Reagents. James Colquhoun Irvine and Walter Norman Haworth (Brit. Pat. 117824, 1918).—In the interaction of sulphuryl chloride and methyl or ethyl alcohol, the formation of an alkyl chlorosulphonate and alkyl sulphate have been observed (Behrend, A., 1877, i, 182; ii, 287), but under suitable conditions the main product is a mixture of alkyl sulphate and alkyl hydrogen sulphate. On distillation under diminished pressure, the alkyl hydrogen sulphate in the mixture undergoes decomposition into sulphuric acid and alkyl sulphate, so that a good yield of the latter is obtained. The sulphuryl chloride may be preformed or may be prepared in situ from sulphur dioxide and chlorine. [See also *J. Soc. Chem. Ind.*, 606A.] D. F. T.

Kephalin. V. Hydrokephalin of the Egg-yolk. P. A. Levene and C. J. West (*J. Biol. Chem.*, 1918, **35**, 285—290. Compare this vol., i, 98).—Hydrokephalin has been isolated in an almost pure state from the sample of hydrolecithin previously suspected of containing it (*loc. cit.*). The raw material was freed from unsaturated compounds by dissolving in chloroform and then pouring into a large excess of ether. It was then subjected to repeated fractional crystallisation from a mixture of equal volumes of chloroform and ethyl methyl ketone, and then from a mixture of chloroform and alcohol (1:2). The final preparation had the correct empirical composition, $C_{41}H_{82}O_8NP$, corresponding with the structure $C_{17}H_{35}\cdot CO\cdot O\cdot CH{<}^{CH_2\cdot O\cdot CO.C_{17}H_{35}}_{CH_2\cdot O\cdot PO(OH)\cdot O\cdot CH_2\cdot CH_2\cdot NH_2}$, which may therefore be regarded as established for the substance. The rotation of the pure substance is $[\alpha]_D^{20}$ in chloroform $+6{\cdot}0°$. H. W. B.

Manufacture of Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 112766, 1918).—Ethylidene acetate is prepared by passing acetylene into a solution of mercuric oxide in glacial acetic acid to which an alkyl sulphate, particularly methylene sulphate, has also been added. [See also *J. Soc. Chem. Ind.*, 606A.] D. F. T.

The Acid Function in the Methenic and Methinic Derivatives. J. GUINCHANT (*Ann. Chim.*, 1918, [ix], **9**, 49—108 109—143; 1918, [ix], **10**, 30—84).—A more detailed account of work already published (compare A., 1895, i, 649; 1896, i, 594 ii, 12, 465). W. G.

Reduction of Aldehydes to Corresponding Alcohols. I. Reduction of Heptaldehyde. P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1918, **35**, 281—283).—The method is essentially the same as that employed for the reduction of esters (Levene and Allen, A., 1917, i, 3). An emulsion of metallic sodium in toluene is first prepared, and a solution of the aldehyde in glacial acetic acid and toluene is slowly added, the mixture being continuously cooled and stirred. The yield is about 60% of the theoretical. *Heptyl phenylcarbamate*, $C_{14}H_{21}O_2N$, prepared by heating the alcohol with an equal weight of phenylcarbimide at 175° for a few minutes crystallises from dilute alcohol in needles, m. p. 60° (corr.). H. W. B.

Effect of Variations in the Available Alkali on the Yield of Acetone in the Oxidation of Butyric Acid with Hydrogen Peroxide. EDGAR J. WITZEMANN (*J. Biol. Chem.*, 1918, **35** 83—100).—When butyric acid is oxidised by means of hydrogen peroxide in dilute solution in the presence of variable amounts of alkali hydroxide, the quantity of acetone recoverable is greatest when the reaction of the system is neutral to faintly acid. As the alkalinity increases, the velocity of oxidation of the butyric acid also increases, but the yield of acetone decreases probably because the acetone itself becomes increasingly susceptible to oxidation with the increasing alkalinity. When dextrose is added to the reaction mixture, the products of oxidation of the dextrose reduce the alkalinity if the supply of alkali is limited, resulting in an increased production of acetone. If, however, there is an excess of alkali, the dextrose exerts a "sparing" action on the butyric acid which is analogous to the "sparing effect" of carbohydrate in the body. H. W. B.

*iso***Phorone.** MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 219—224. Compare A., 1911, i, 939, and following abstracts).—The author has prepared and purified, as far as possible, by distillation a large quantity of *iso*phorone, and from it has obtained two oximes, one having m. p. 70—73° and the other m. p. 97—100°. When boiled with alcoholic potassium hydroxide, the oxime, m. p. 73°, is slowly converted into its isomeride. Only one semicarbazone, m. p. 187°, was obtained. W. G.

Homophorone. MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 224—229. Compare A., 1911, i, 939, and preceding and succeeding abstracts).—From the fraction 160—200° obtained in the fractionation of crude *iso*phorone, *homophorone*, $C_9H_{14}O$, has been isolated as a colourless liquid, b. p. 192—194°, giving only one *oxime*, m. p. 87—88°, which, unlike those from *iso*phorone, is easily decomposed by hydrochloric acid, but is not transformed into an isomeride by potassium hydroxide. *Homophorone semicarbazone* has m. p. 206°. W. G.

Action of Dilute Sulphuric Acid on Pure Pinacone. MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 229—232. Compare preceding abstracts).—A theoretical discussion of work already published (compare A., 1911, i, 347, 939). W. G.

The Conversion of Lævulose-diphosphoric Acid into the Corresponding Monophosphoric Acid. CARL NEUBERG (*Biochem. Zeitsch.*, 1918, **88**, 432—436).—This conversion can be brought about by gentle warming of a salt with *N*-hydrochloric acid or oxalic acid. The calcium salt of the monophosphoric acid has the formula $C_6H_{11}O_9PCa,H_2O$, and the barium salt $C_6H_{11}O_9PBa,H_2O$. The monophosphate can be fermented by living yeast, whereas the diphosphate cannot. S. B. S.

Oxidation Product of Creatine. LOUIS BAUMANN and THORSTEN INGVALDSEN (*J. Biol. Chem.*, 1918, **35**, 277—280).—After the removal of carnosine from an aqueous extract of muscle by means of mercuric acetate and sodium carbonate, a glistening, flaky substance is gradually precipitated from the filtrate. By decomposition of the precipitate with hydrogen sulphide and recrystallisation from water, *a-methylguanidinoglyoxylic acid*,

$$NH_2\cdot C(NH)\cdot NMe\cdot CO\cdot CO_2H,2H_2O,$$

is obtained in the form of glistening flakes, m. p. 203—204°. The new compound is evidently produced from creatine by the oxidising action of mercuric acetate, and can also be prepared directly by the oxidation of either pure creatine or creatinine. It is somewhat toxic, 0·15 gram injected into a guinea-pig causing death in two hours. Its injection into a dog increases the elimination of creatine in the urine. H. W. B.

Hypochlorous, Hypobromous, and Hypoiodous Amides. ÉTIENNE BOISMENU (*Ann. Chim.*, 1918, [ix], **9**, 144—188).—A résumé of work already published (compare A., 1911, i, 957; 1912, i, 15, 97). W. G.

Action of the Chlorides of Phosphorus on Phenolsulphonic Acids. II. RICHARD ANSCHÜTZ and EUGEN MOLINEUS (*Annalen*, 1918, **415**, 51—64. Compare A., 1908, i, 83).—*p*-Chlorosulphonylphenyl dichloro-orthophosphate,

$$SO_2Cl\cdot C_6H_4\cdot O\cdot POCl_2,$$

is converted by heating with an equimolecular quantity of phosphorus pentachloride at 180° into *p*-chlorophenyl dichloro-orthophosphate, and the latter, treated similarly at 250°, is converted quantitatively into *p*-dichlorobenzene. p-*Chlorosulphonylphenyl metaphosphate*, $SO_2Cl\cdot C_6H_4\cdot O\cdot PO_2$, obtained by heating the corresponding dichloride with the calculated quantity of water (weighed in the form of anhydrous oxalic acid), forms transparent crystals and is converted into *p*-chlorosulphonylphenyl dihydrogen phosphate by exposure to moisture in the air.

Potassium p-*acetoxybenzenesulphonate*, $SO_3K\cdot C_6H_4\cdot OAc$, crystals, prepared by heating potassium phenol-*p*-sulphonate with acetic anhydride at 150°, is converted by phosphorus pentachloride on the water-bath into p-*acetoxybenzenesulphonyl chloride*, crystals, m. p. 78°, b. p. 148°/12 mm., which reacts in ethereal solution with aniline, *p*-toluidine, and piperidine (2 mols.) to form the *anilide*, $OAc\cdot C_6H_4\cdot SO_2\cdot NHPh$, m. p. 126—127°, p-*toluidide*, m. p. 98—99°, and *piperidide*, m. p. 115—116°, respectively. These three substances are converted by heating with alcohol (the first requires potassium hydroxide in addition) into *phenol*-p-*sulphonanilide*, needles, m. p. 137—138°, -p-*toluidide*, needles, m. p. 151—152°, and -*piperidide*, m. p. 132—133°, respectively.

When heated with carbon tetrachloride and phosphorus pentachloride at 180—200°, 2:6-dibromo-4-chlorosulphonylphenyl dichloro-orthophosphate (*loc. cit.*) is converted into 4-*chloro*-3:5-*dibromobenzenesulphonyl chloride*, $C_6H_2ClBr_2\cdot SO_2Cl$, crystals, m. p. 94·5°, b. p. 203—208°, and this is converted into 1:2:4:6-tetrachlorobenzene by phosphorus pentachloride at 200°. C. S.

Sulphonylides. RICHARD ANSCHÜTZ (*Annalen*, 1918, **415**, 64—97. Compare A., 1912, i, 852).—[With (FRL.) CLARA ZYMANDL.]—o-*Chlorosulphonylphenyl dichloro-orthophosphate*,

$$SO_2Cl\cdot C_6H_4\cdot O\cdot POCl_2,$$

yellow oil, b. p. 185°, obtained from sodium phenol-*o*-sulphonate and phosphorus pentachloride (rather more than 1 mol.), is converted by heating with phosphorus pentachloride at 150° into o-*chlorophenyl dichloro-orthophosphate*, pale yellow oil, b. p. 135—137°/12 mm., which yields *o*-chlorophenol by boiling with water, and *o*-dichlorobenzene by heating with phosphorus pentachloride at 250°.

Sodium acetoxybenzene-o-*sulphonate*, $OAc\cdot C_6H_4\cdot SO_3Na$, obtained by heating the phenol-*o*-sulphonate with acetic anhydride, is converted by phosphorus pentachloride into *acetoxybenzene*-o-*sulphonyl chloride*, colourless crystals, m. p. 73·2—73·9°, which yields the *sulphonanilide*, $OAc\cdot C_6H_4\cdot SO_2\cdot NHPh$, m. p. 106—107°, and *sulphon*-p-*toluidide*, leaflets, m. p. 116—117°, by treatment with aniline and *p*-toluidine respectively; these are hydrolysed, the latter by boiling alcohol alone, the former by the calculated quantity of boiling alcoholic potassium hydroxide, yielding *phenol*-o-*sulphonanilide*, $OH\cdot C_6H_4\cdot SO_2\cdot NHPh$, leaflets, m. p. 126·5—127·5°, and *phenol*-o-*sulphon*-p-*toluidide*, leaflets, m. p. 124—125°,

each of which develops a violet coloration with alcoholic ferric chloride. Phenylene-*o*-sulphonylide is produced when an ethereal solution of acetoxybenzene-*o*-sulphonyl chloride is treated with gaseous ammonia or with an ethereal solution of diethylamine, acetyl chloride being eliminated.

[With L. HODENIUS.]—*Sodium 4-acetoxytoluene-3-sulphonate*, prepared from the *p*-cresolsulphonate and acetic anhydride at 150°, is converted by phosphorus pentachloride into *4-acetoxytoluene-3-sulphonyl chloride*, m. p. 55—56°, b. p. 165—170°/20 mm., which yields tolylene-3:4-sulphonylide by treatment with ethereal ammonia or diethylamine. The following three compounds are prepared by methods similar to the preceding: *sodium 4-acetoxytoluene-3:5-disulphonate*, *4-acetoxytoluene-3:5-disulphonyl chloride*, crystals, m. p. 115°, and *4-acetoxytoluene-3:5-disulphonyldiethylamide*, $OAc\cdot C_6H_2Me(SO_2\cdot NEt_2)_2$, crystals, m. p. 150°.

Tolylene-3:4-sulphonylide-5:5'-disulphonic acid,

$$SO_3H\cdot C_6H_2Me{<}{}^{O\cdot SO_2}_{SO_2\cdot O}{>}C_6H_2Me\cdot SO_3H,3H_2O,$$

is prepared by treating *p*-cresol-3:5-disulphonic acid with fuming sulphuric acid (60% SO_3), finally at 100° with the further addition of the fuming acid, and recrystallising the precipitate from dilute nitric acid; it forms a *potassium* salt, long needles with $5\frac{1}{2}H_2O$, *silver* salt, colourless needles, and *ferric* salt, colourless needles, and, when anhydrous, reacts with phosphorus pentachloride to form *tolylene-3 : 4-sulphonylide-5 : 5'-disulphonyl chloride*, crystals, decomp. about 280°, which is stable to boiling water.

1:4-tert.-*Butylphenol-3-sulphonic acid*, $CMe_3\cdot C_6H_3(OH)\cdot SO_3H$, is obtained by heating *p-tert*.-butylphenol with pure sulphuric acid at 70—80°. Its *sodium* salt, anhydrous crystals, yields by acetylation *sodium 4-acetoxy-1-*tert.*-butylbenzene-3-sulphonate*, which is converted by phosphorus pentachloride on the water-bath into *4-acetoxy-1-*tert.*-butylbenzene-3-sulphonyl chloride*, crystals, m. p. 103°. tert.-*Butylphenylene-3:4-sulphonylide*,

$$CMe_3\cdot C_6H_3{<}{}^{O\cdot SO_2}_{SO_2\cdot O}{>}C_6H_3\cdot CMe_3,$$

microscopic needles, m. p. 301—302°, is obtained by the action of phosphoryl chloride on 1:4-*tert*.-butylphenol-3-sulphonic acid. The following amyl compounds are prepared like the corresponding butyl compounds: 1:4-tert.-*amylphenol-3-sulphonic acid* and its *sodium* salt, *sodium 4-acetoxy-1-*tert.*-amylbenzene-3-sulphonate*, *4-acetoxy-1-*tert.*-amylbenzene-3-sulphonyl chloride*, b. p. 142—146°/14 mm., and tert.-*amylphenylene-3:4-sulphonylide*, colourless crystals, m. p. 228—229°.

The substance obtained by Schiff (*Annalen*, 1875, **178**, 187) by treating sulphotannic acid or its acetyl derivative with acetic anhydride is *5:6-diacetoxy-o-phenylenesulphonylide*.

[With (FRL.) MARIA MAXIM.]—*Sodium 2-acetoxynaphthalene-1-sulphonate*, faintly red needles, prepared by acetylating the

naphtholsulphonate, is converted by phosphorus pentachloride in the presence of chloroform into *2-acetoxynaphthalene-1-sulphonyl chloride*, crystals, m. p. 115·5°, which cannot be converted into a sulphonylide by means of pyridine, neither can *2-naphthol-1-sulphonyl chloride*, colourless needles, m. p. 124°, obtained by hydrolysing the preceding acetyl derivative with warm dilute sodium hydroxide. The following derivatives of 1-naphthol-2-sulphonic acid are obtained by methods similar to the preceding: *potassium 1-acetoxynaphthalene-2-sulphonate*, colourless prisms, *1-acetoxynaphthalene-2-sulphonyl chloride*, crystalline powder, m. p. 87·5°, *1-acetoxynaphthalene-2-sulphonamide*, stout, yellow needles without a sharp m. p., and the corresponding *sulphonanilide*, $OAc\cdot C_{10}H_6\cdot SO_2\cdot NHPh$, crystals, m. p. 157·5°, and *sulphon-p-toluidide*, m. p. 135·5°. *2 : 1-Naphthylenesulphonylide*,

$$C_{10}H_6<\begin{matrix}O\cdot SO_2\\SO_2\cdot O\end{matrix}>C_{10}H_6,$$

colourless, crystalline powder, decomp. above 300°, is obtained (1) by adding phosphoryl chloride with cooling to a mixture of potassium 1-naphthol-2-sulphonate, pyridine, and chloroform, (2) by shaking 1-acetoxynaphthalene-2-sulphonyl chloride with pyridine at the ordinary temperature.

Sodium 2-naphthol-1-sulphonate yields 2-naphthol-1 : 3 : 6 : 7-tetrasulphonic acid by heating with four parts of fuming sulphuric acid (40% SO_3) at 120—130° for eight hours, but when heated with five parts for two days is converted into a substance, colourless crystals, which appears to be *3 : 2-naphthylenesulphonylide-1 : 6 : 7 : 1′ : 6′ : 7′-hexasulphonic acid* (*sodium* salt, $C_{20}H_6O_{24}S_8Na_6$, colourless, prismatic needles).

Acetylisethionyl chloride, $OAc\cdot CH_2\cdot CH_2\cdot SO_2Cl$, b. p. 130—132°/14 mm., obtained, together with β-chloroethylsulphonyl chloride by heating potassium acetylisethionate with phosphorus pentachloride on the water-bath, cannot be converted into diethylenesulphonylide by means of ammonia or diethylamine; the sulphonylide also cannot be prepared from isethionic acid and phosphoric oxide or phosphoryl chloride. C. S.

The Stereochemistry of Quinquevalent Nitrogen. VI. SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 151—159).—After reviewing the state of knowledge with respect to the decomposition of quaternary ammonium compounds by heat and the various proposals for the representation of the spatial distribution of the valencies of the quinquevalent nitrogen atom, the author agrees with the assumption that four of the valencies possess the same value, whilst the fifth is of a different nature and suggests an extension of the views of Meisenheimer (A., 1909, i, 20; 1912, i, 25; 1913, i, 595) on the structure of the quinquevalent nitrogen atom. The atom is regarded as situate at the centre of a tetrahedron, at the corners of which the four radicles are disposed; the fifth and negative radicle is in an outer zone, and occupies a fixed

position which, however, may vary with the manner of formation of the ammonium compound, thus influencing the optical rotation of the substance, but leaving the chemical properties unaffected. By this hypothesis, the existence of two modifications of *d*-phenylbenzylmethylallylammonium iodide (Komatsu, A., 1915, i, 1054) is explained. D. F. T.

The Solidifying and Boiling Points of Phenol and the Cresols. J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1918, **37**, 268—272T).—The authors have determined the freezing-point and boiling-point curves of mixtures of phenol, and *o*-, *m*-, and *p*-cresols taken in pairs. Phenol and *o*-cresol show a continuous freezing-point curve with a minimum corresponding nearly with equimolecular proportions, but no eutectic point. The boiling-point curve is nearly a straight line. The phenol–*m*-cresol freezing-point curve *has two minimum (eutectic) points, and between them a maximum* at 17°, indicating the formation of a molecular compound of the formula $C_6H_5 \cdot OH, 2C_7H_7 \cdot OH$. The compound forms a eutectic with phenol at 10·2° and with *m*-cresol at −4°. The boiling-point curve is a normal binary mixture curve. The freezing-point curve for phenol and *p*-cresol shows a sharp eutectic with equimolecular proportions of the constituents, whilst the boiling-point curve is normal.

When the cresols are taken in pairs, those containing *m*-cresol show the most complicated curves. The freezing-point curve of *m*- and *p*-cresols shows a maximum at 20% *p*-cresol, but only one eutectic, a 50% mixture, was detected. The curve for *o*- and *m*-cresols shows two distinct breaks, but no maximum, and the existence of a compound cannot be inferred.

The results show that many different mixtures of phenol and the cresols have the same freezing point. It is unsafe to consider a sample of "cresylic acid" free from phenol because it yields a distillate which does not freeze when immersed in ice-water.

E. H. R.

Nitro-derivatives of Guaiacol. Fanny Pollecoff and Robert Robinson (T., 1918, **113**, 645—656).—The nitration of 4-nitroguaiacol yields 4:6-dinitroguaiacol, and of 4-nitroguaiacyl acetate a mixture of the 3:4- and the 4:5-dinitro-derivatives in undetermined proportions. By nitration, guaiacol carbonate yields successively 5-*nitro-2-methoxyphenyl carbonate*,

$$(NO_2 \cdot C_6H_3 \cdot OMe)_2CO_3,$$

colourless needles, m. p. 133°, and 3:5-*dinitro-2-methoxyphenyl carbonate*, colourless needles, m. p. 148°, which yield on hydrolysis 5-nitroguaiacol and 3:5-*dinitroguaiacol*, pale yellow needles, m. p. 80°, respectively. The nitration of 5-nitroguaiacol yields 5:6-*dinitroguaiacol*, yellow prisms, m. p. 205—208° (decomp.) (*acetate*, colourless needles, m. p. 124—125°), together with the 4:5-isomeride as by-product; the former, after reduction and treatment with phenanthraquinone, yields 1-*hydroxy-2-methoxyphenanthra-*

phenazine, golden-yellow needles, m. p. 224°. 4:5-*Dinitroguaiacol* forms pale yellow needles, m. p. 172° (*acetate*, colourless, prismatic needles, m. p. 123—124°, sintering at 114°), and is converted as above into 2-*hydroxy-3-methoxyphenanthraphenazine*, yellow threads, m. p. 239—240°.

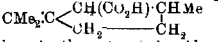
The further nitration of 4:6-, 5:6-, or 4:5-dinitroguaiacol is not practicable, but the 3:5-isomeride readily yields 3:5:6-*trinitroguaiacol*, yellow prisms, m. p. 129° (decomp.), as the sole product, which forms a characteristic *pyridine* salt, $C_7H_5O_8N_3,C_5H_5N$, yellow needles, m. p. 180°, 185°, or 194—195° (decomp.; according to the rate of heating), and yields 3:5:6-*trinitroveratrole*, pale yellow needles, m. p. 174°, by methylation. The last compound is converted into 3:5-*dinitro*-2:6-*diaminoanisole*, garnet needles, m. p. 237°, by boiling methyl-alcoholic aqueous ammonia, and into 4:6-*dinitro*-1:2:3-*trimethoxybenzene*, pale yellow needles, m. p. 85°, by boiling methyl-alcoholic potassium hydroxide. C. S.

Synthesis of Elemicin and of *iso*Elemicin. F. MAUTHNER (*Annalen*, 1917, **414**, 250—255).—2:6-*Dimethoxyphenyl allyl ether*, $C_6H_3(OMe)_2\cdot O\cdot CH_2\cdot CH\colon CH_2$, a colourless oil, b. p. 140—141°/14 mm., prepared from allyl bromide and pyrogallol 2:6-dimethyl ether in boiling acetone in the presence of potassium carbonate, is converted by heating at 220° in a few minutes into 2:6-*dimethoxy-4-allylphenol*, $OH\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH\colon CH_2$, b. p. 168—169°/11 mm., which yields by methylation with methyl sulphate and 10% sodium hydroxide solution 3:4:5-trimethoxyallylbenzene, identical with elemicin. The position of the allyl group is proved by oxidising the substance in acetone to gallic acid trimethyl ether by potassium permanganate, and of the double linking by the decomposition of the ozonide by water, whereby homogallaldehyde trimethyl ether is obtained. By heating with alcoholic potassium hydroxide, the synthetic elemicin is converted into *iso*elemicin (3:4:5-trimethoxypropenylbenzene), the ozonide of which yields gallaldehyde trimethyl ether by decomposition with water. [See *J. Soc. Chem. Ind.*, October.] C. S.

Synthesis by means of Sodamide. VIII. Phenyldimethylethyl Alcohol, Benzyl-, *o*-, *m*-, and *p*-Methylbenzyl- and *p*-Methoxybenzyl-dimethylethyl Alcohols. ALBIN HALLER and EDOUARD BAUER (*Ann. Chim.*, 1918, [ix], **9**, 5—24).—A résumé of work already published (compare A., 1911, i, 726; 1913, i, 168, 488; 1914, i, 418). W. G.

Terpenes and Ethereal Oils. CXXI. Pulegenic Acid and the Conversion of Carvone into Pulegenic Acid. O. WALLACH (*Annalen*, 1917, **414**, 233—243).—An improved method of preparing pulegenic acid is to shake pulegone dibromide with aqueous potassium hydroxide for one hour at the ordinary temperature, and then for three hours at 100°. Unchanged pulegone and methyl*cyclo*hexanone are removed by steam, and pulegenic acid is

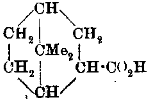
extracted by ether from the somewhat concentrated, acidified residual *solution*.

Like other substances containing a semicyclic linking, pulegenic acid,  (and also its amide), is difficult to reduce to the saturated acid, which, however, can be obtained as follows: hydrogen chloride is added on to methyl pulegenate, and then removed again with simultaneous hydrolysis. The product is a mixture of ordinary pulegenic acid and an isomeride. By distillation under ordinary pressure, the former is converted into pulegene, whilst the latter distils at 256—260° with slight decomposition. It is converted into its amide, m. p. 152°, which is reduced easily by hydrogen and colloidal palladium to dihydropulegenamide, m. p. 150—151° (Eykman gives 147°), from which dihydropulegenic (1-methyl-3-*iso*propyl*cyclo*pentane-2-carboxylic) acid, b. p. 139°/12 mm., D^{24} 0·9600, n_D 1·4524, is readily obtained. An alternative and more convenient method is to heat methyl hydrochloropulegenate with aniline, to reduce the resulting unsaturated ester by Skita's method, and to hydrolyse the product.

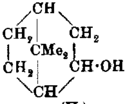
Dihydropulegenamide is converted by Hofmann's method into a *base*, presumably *2-amino-1-methyl-3-*iso*propyl*cyclo*pentane*, which forms an *acetyl* derivative, $C_{11}H_{21}ON$, m. p. 132°, and a *carbamide*, $C_{10}H_{20}ON_2$, m. p. 190°.

[With WOLFGANG VON RECHENBERG.]—The conversion of the 6-ring in carvone into the 5-ring of pulegenic acid, and the formation of this acid from dihydrocarvenolic acid, have been effected as follows. Dihydrocarvenolide, prepared from *d*-carvone, is hydrolysed by potassium hydroxide and boiling amyl alcohol, and the resulting dihydrocarvenolic acid, m. p. 87°, is converted by methyl-alcoholic hydrogen chloride at 0° into a saturated, chlorinated ester, m. p. 15—16°, b. p. 114°/12 mm., which yields pulegenic acid, b. p. 142—145°/11 mm., D^{20} 0·9975, n_D 1·4747, $[\alpha]_D^{20}$ +32·67° in ether, by boiling with alcoholic sodium methoxide and subsequent hydrolysis. The pulegenic acid thus obtained is converted into its amide, m. p. 152° (occasionally 123°; conditions of formation unknown), which yields dihydropulegenamide, m. p. 150—151°, by reduction as above. C. S.

Total Synthesis of α-Fenchenylanic Acid (*alloapo*-**Camphanecarboxylic Acid**), **and a New Type of Decomposition of Ozonides.** GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennicae, A.*, [x], **18**, 1—7; from *Chem. Zentr.*, 1918, i, 623—624).—In the ozonisation of α-fenchene (Komppa and

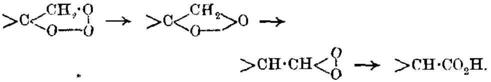


(I.)



(II.)

Hintikka, A., 1914, i, 557; Komppa and Roschier, A., 1917, i, 466), the authors have obtained α-fenchocamphorone and fenchenylanic acid (annexed formula, I). The constitution of the latter is now confirmed by a synthesis of the acid from *dl*-α-fenchocamphorone, which, on reduction with sodium and alcohol, yields dl-α-*fencho-camphorol* (annexed formula, II), needles, m. p. 122—124°, b. p. 203°; from this, by conversion into the corresponding dl-α-*fencho-camphoryl chloride*, $C_9H_{15}Cl$, m. p. approx. 24—25°, b. p. 74·5°/13 mm., an organo-magnesium compound is obtainable which reacts with carbon dioxide, with formation of *dl*-α-fenchenylanic acid (*alloapo*camphanecarboxylic acid). This result proves that the decomposition of the ozonide of α-fenchene does not entirely follow the normal course, but that to some extent decomposition occurs without scission of a carbon atom, possibly as indicated by the scheme:



D. F. T.

Action of Nitrous Acid on Methyl *p*-Dimethylamino-benzoate and *p*-Dimethylaminobenzaldehyde. (Reactions of *tert.*-Amines, and a Contribution to the Subject of Steric Hindrance). FRANZ KLAUS and OSKAR BAUDISCH (*Ber.*, 1918, **51**, 1036—1048. Compare A., 1907, i, 131).—When methyl *p*-dimethylaminobenzoate is treated with sodium nitrite and hydrochloric acid at −5°, it yields methyl 3-nitro-4-dimethylamino-benzoate, m. p. 75° (Reverdin and Delétra, A., 1906, i, 273), and *methyl* p-*nitrosomethylaminobenzoate*, $CO_2Me\cdot C_6H_4\cdot NMe\cdot NO$, which crystallises in satiny needles, m. p. 115·5°. The identity of the latter compound is established by its reactions (*A*) and synthesis (*B*). *A*.—It yields *p*-nitrosomethylaminobenzoic acid, m. p. 202°, on hydrolysis with sodium hydroxide; it gives *p*-methylaminobenzoic acid, m. p. 163°, and its methyl ester, m. p. 95·5° (not 73—75°, as Johnston stated, P., 1905, 156), when boiled with aqueous and methyl-alcoholic hydrochloric acid, respectively. *B*.—Methyl *p*-methylaminobenzoate is prepared by esterifying the acid or by hydrolysing *p*-nitrosomethylaminobenzoic acid with methyl-alcoholic hydrogen chloride, and is treated with nitrous acid, or methyl anthranilate is methylated by means of methyl sulphate and then nitrosated

p-Dimethylaminobenzaldehyde behaves in a similar manner towards nitrous acid, the products being p-*nitrosomethylamino-benzaldehyde*, $CHO\cdot C_6H_4\cdot NMe\cdot NO$, pale straw-yellow crystals, m. p. 78°, 3-nitro-4-dimethylaminobenzaldehyde, m. p. 105°, and *p*-nitrosodimethylaniline. J. C. W.

Amino-oxides. OSKAR BAUDISCH (*Ber.*, 1918, **51**, 1048—1058) —The action of permonosulphuric acid on *p*-dimethylaminobenzoic

acid leads to the formation of the sulphate of an amino-oxide. The free amino-oxide can be obtained by precipitation with potassium acetate, and it is found to give a number of characteristic salts, presumably of the oxonium type, and to behave in an interesting manner towards nitrous and sulphurous acids.

p-*Dimethylaminobenzoic acid* N-*oxide*, $CO_2H\cdot C_6H_4\cdot NMe_2\colon O$, crystallises in very long, prismatic needles, m. p. 192·5°, gives formaldehyde when heated, and yields the following salts: *sulphate*, feathery groups of needles, as much as an inch long, with $1H_2O$, m. p. 160° (decomp.); *hydrochloride*, snow-white needles, m. p. 184°; *aurichloride*, reddish-yellow, m. p. 136°; *picrate*, yellow needles, m. p. 155°; *platinichloride*, pink needles, m. p. 155—156°; *ferrocyanide*, white needles. When a solution of the sulphate is saturated with sulphur dioxide, it suddenly becomes green and deposits white crystals of 4-*dimethylamino*-3-*sulphobenzoic acid*, $CO_2H\cdot C_6H_3(NMe_2)\cdot SO_3H$, m. p. 279—280°, the mother liquor containing *p*-dimethylaminobenzoic acid. A solution in dilute hydrochloric acid, when treated with sodium nitrite, yields some *p*-nitrodimethylaniline, a trace of *p*-nitrosodimethylaniline, but chiefly 3-nitro-4-dimethylaminobenzoic acid (A., 1907, i, 132). This has been reduced by means of stannous chloride to 3-*amino*-4-*dimethylaminobenzoic acid*, which crystallises in pale pink leaflets, m. p. 152—153°, and forms a *hydrochloride*, long needles, m. p. 237°, solutions of which give a deep red coloration and crystalline precipitate when warmed with ferric chloride.

p-*Diethylaminobenzoic acid* N-*oxide* has been prepared in a similar manner. It crystallises in long needles, m. p. 170—171°, evolves acetaldehyde on heating, and yields the following salts: *sulphate*, $1H_2O$, long, white needles, m. p. 173·5—174·5°; *hydrochloride*, m. p. 162·5—163·5°; *platinichloride*, m. p. 178°; *aurichloride*, m. p. 177°; *picrate*, m. p. 169—171°; and *hydrogen ferrocyanide*, snowy leaflets. Sulphurous acid reduces it to *p*-diethylaminobenzoic acid and 4-*diethylamino*-3-*sulphobenzoic acid*, m. p. 308—310°, and nitrous acid converts it into a mixture of *p*-nitrosoethylaniline, *p*-nitrosoethylaminobenzoic acid, 3-nitro-4-ethylaminobenzoic acid, 3-nitro-4-diethylaminobenzoic acid, and *p*-nitrodiethylaniline. J. C. W.

***iso*Valeric Acid, and its Abnormal Behaviour in the Perkin Synthesis.** ALFRED SCHAARSCHMIDT, E. GEORGEACOPOL and JOHANN HERZENBERG (*Ber.*, 1918, **51**, 1059—1074).—When *iso*valeric acid is applied to aldehydes under the conditions of the Perkin reaction, the main products are not the expected unsaturated acids, but the ethylenes derived from these by loss of carbon dioxide. The condensations take place at unusually low temperatures, so low, in fact, that it is doubtful if the unsaturated acids represent an intermediate stage at all. The authors believe that the primary α-hydroxy-acid first loses carbon dioxide and then water rather than suffer decomposition in the reverse order.

The results of the experiments described are summarised as

follows, the weights, in grams, being given in brackets: Benzaldehyde (15), *iso*valeric anhydride (50), sodium *iso*valerate (45), heated for thirty hours at 100°, gave α-iso*propylcinnamic acid*, $CHPh:CPr^{\beta}\cdot CO_2H$ (1·9), leaflets, m. p. 118·5°, and α-phenyl-γ-methyl-Δ^{α}-butene, $CHPh:CHPr^{\beta}$ (9·3). The same reagents, in the proportions 50 : 175 : 150, heated for six hours at 150°, gave the same hydrocarbon (46) (Schramm, A., 1883, 1094; Kunckell, A., 1904, i, 386; Klages, *ibid.*, 569). Benzaldehyde (15), acetic anhydride (55), and sodium *iso*valerate (45), heated for thirty hours at 100°, gave the same hydrocarbon (0·6), but no acid. Benzaldehyde (15), *iso*valeric anhydride (55), and sodium acetate (45), heated for ten hours at 150°, gave the hydrocarbon (3·2) and ordinary cinnamic acid (11).

Furfuraldehyde (50), *isovaleric anhydride* (150), *and sodium* *iso*valerate, heated for five hours at 150°, gave α-*2-furyl-γ-methyl-Δ^{α}-butene*, $C_4H_3O\cdot CH:CHPr^{\beta}$ (32), a pleasant-smelling, pale yellow oil, b. p. 64—66°/13 mm., 165—167°/atm., and a trace of β-*2-furyl-α-*iso*propylacrylic acid*, $C_4H_3O\cdot CH:CPr^{\beta}\cdot CO_2H$ (0·5), colourless leaflets, m. p. 114°. Furfuraldehyde (25), acetic anhydride (250), and sodium *iso*valerate (75), heated for seven hours at 150°, gave no hydrocarbon, but 6 grams of β-2-furylacrylic acid, *m. p.* 140°.

Anisaldehyde (50), *iso*valeric anhydride (175), and sodium *iso*valerate (150), heated for eight hours at 150°, gave α-*p*-methoxyphenyl-γ-methyl-Δ^{α}-butene (22) (Moureu and Chauvet, A., 1897, i, 404) and p-*methoxy-α-*iso*propylcinnamic acid*,

$$OMe\cdot C_6H_4\cdot CH:CPr^{\beta}\cdot CO_2H,$$

needles, m. p. 134—135°.

No definite results were obtained with *o*-nitrobenzaldehyde, salicylaldehyde, cinnamaldehyde, or *iso*butaldehyde. The aliphatic aldehyde gave no hydrocarbon or acid, whilst the others reacted very sluggishly. J. C. W.

The Double Acid from Normal and *allo*-Cinnamic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1230—1233).—The double acid can be prepared (1) by crystallisation from a solution saturated with respect to both acids, and (2) by exposing a dilute solution of sodium cinnamate (about 1%) to light for several months, evaporating to dryness, acidifying the residue with hydrochloric acid, and extracting the organic acids with hot light petroleum; the cold extract ultimately yields crystals of the double acid. A saturated solution of the two acids in equilibrium with the *allo*-acid of m. p. 42°, inoculated with the *allo*-acid of m. p. 58° or 68°, soon crystallises, and solutions are obtained which are in equilibrium with these two modifications. If these solutions are allowed to evaporate, the double acid separates, together with the modification of the *allo*-acid used for inoculation. The double acids obtained from these solutions consist of 50% of normal acid and 50% of *allo*-acid, all melt in the same way, sintering at about 56° and being completely molten

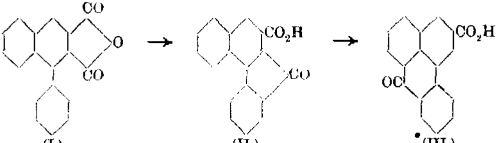
at about 90°, and are all proved to be identical in the following way. An aqueous solution saturated with the normal acid and the *allo*-acid at the ordinary temperature, and in equilibrium with the *allo*-acid of m. p. 42°, was prepared, and to portions of this solution crystals of the double acids were added. They produced no effect whatever. Had the various double acids been different, that produced in the presence of *allo*-acid of m. p. 58° (or 68°) should have brought about crystallisation of the *allo*-acid of m. p. 58° (or 68°) and of the corresponding double acid.

The identity of the various double acids supports Biilmann's view that the three modifications of *allo*-cinnamic acid are trimorphous, and is opposed to Stobbe and Schönburg's theory that they are three different chemical individuals. C. S.

α-Naphthoicsulphinide. KURT KALCHER (*Annalen*, 1917, **414**, 244—249).—α-Cyanonaphthalene-β-sulphonyl chloride, m. p. 143—144° (Friedländer and Woroshzow, A., 1912, i, 293, give 141—142°), is converted by ammonia gas in hot, dry benzene solution into *α-cyanonaphthalene-β-sulphonamide*, monoclinic crystals, decomp. 300—340°, which is converted by boiling $N/10$-sodium hydroxide ($1\frac{1}{4}$ mols.) and subsequent acidification into *α-naphthoicsulphinide*, $C_{10}H_6<\substack{CO\\SO_2}>NH$, clusters of small prisms, m. p. 244°, together with the sodium salt of an acidic by-product. The sulphinide, which is best purified through its *sodium* salt, long, flattened needles, has a bitter taste and forms a *methyl* derivative, leaflets, m. p. 220—221°, which yields methylamine by hydrolysis with 35% hydrochloric acid at 150°. The nature of the acidic by-product has not been established. C. S.

A New Benzanthrone Synthesis. II. Transformation of 1-Phenylnaphthalene-2 : 3-dicarboxylic Anhydride into Benzanthronecarboxylic Acid. ALFRED SCHAARSCHMIDT and ERNST KORTEN (*Ber.*, 1918, **51**, 1074—1082. Compare A., 1917, i, 274).—1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride (I) was first converted into 3 : 4-benzofluorenone-1-carboxylic acid (II) by prolonged treatment with concentrated sulphuric acid at the ordinary temperature (Stobbe, A., 1907, i, 766), and recently by means of aluminium chloride in benzene (A., 1916, i, 47). In order to hasten the older process, the authors have tried the effect of heating the anhydride with 91% sulphuric acid at 155°, the mixture being stirred for three hours. Under these conditions, two different products are obtained, namely, benzanthronecarboxylic acid, III (*loc. cit.*), which is insoluble in boiling water, and a soluble, red *sulphonic acid*, $C_{18}H_{10}O_6S$. This has the structure of a fluorenone, for it yields an oxime, and since it is non-fluorescent in sulphuric acid, it is most probably a derivative of 3 : 4-benzofluorenone-1-carboxylic acid. The same products are obtained by

treating this acid in the above manner, and the chief reaction can therefore be represented thus:



(I.) (II.) (III.)

It illustrates the rupture of a weak five-membered ring and the establishment of a six-membered system. A similar change is suffered by 3:4-benzofluorenone itself when heated with sulphuric acid, for fluorescence is developed, but in this case the chief effect is sulphonation.

The imide of the original acid exhibits the same phenomenon most readily. 1-*Phenylnaphthalene*-2:3-*dicarbimide*, m. p. 249°, is obtained by heating the anhydride with ammonia at 240—250°. When warmed with 96% sulphuric acid at 75° for five minutes, this yields 3:4-benzofluorenone-1-carboxylic acid and its orange-red *amide*, m. p. 281—282°, whilst at 130°, *benzanthronecarboxamide*, m. p. 306°, is formed. This has been prepared from the acid (III) for comparison, and it exhibits a brilliant yellowish-green fluorescence in sulphuric acid. J. C. W.

A New Benzanthrone Synthesis. III. ALFRED SCHAARSCHMIDT and E. GEORGEACOPOL (*Ber.*, 1918, **51**, 1082—1087. Compare A., 1917, i, 274).—As already suggested, experiments prove that when 3:4-benzofluorenone is fused with potassium hydroxide, it yields the salts of 1-phenylnaphthalene-2-carboxylic acid and *o*-α-*naphthylbenzoic acid*. The free acids may be separated by means of methyl alcohol, from which the latter acid, being only moderately soluble, crystallises in colourless rhombohedra, m. p. 161·5°. If the acids are treated with phosphorus pentachloride and then aluminium chloride, the former yields 3:4-benzofluorenone again, whilst the latter gives benzanthrone. This ketone may also be prepared by the distillation of the ammonium salt of its carboxylic acid. J. C. W.

Oxidation of Santonin by means of Organic Per-acids. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 117—121; *Gazzetta*, 1918, **48**, i, 248—253).—Oxidation of santonin by means of perbenzoic or peracetic acid results in the formation of two products: (1) *iso*Artemisin or δ-oxysantonin. (2) ε-*Oxysantonin*, $C_{15}H_{18}O_4$, which crystallises in bundles of acicular prisms, m. p. 154°, at which temperature it is stable; it does not react with phenylcarbimide, and yields only a *monophenylhydrazone*,

$$C_{15}H_{18}O_3{:}N_2HPh,$$

m. p. about 280°. ε-Oxysantonin is not altered by aqueous alkali

hydroxide, but the lactone ring of its molecule may be opened by means of hot alcoholic sodium ethoxide, which changes the colour to blood-red with a transitory green fluorescence; the *acid*, $C_{15}H_{20}O_5$, thus obtained forms crystals, m. p. about 100°, and when heated with dilute sulphuric acid gives the original oxysantonin.

Treatment of ε-oxysantonin with concentrated hydrochloric acid in the cold yields a new *chlorosantonin*, $C_{15}H_{17}O_3Cl$, which forms crystals, m. p. about 196°, and is transformed into ε-oxysantonin by either cold alcoholic potassium hydroxide or boiling aqueous alcohol; by zinc dust and a few drops of acetic acid in alcoholic solution, it is converted into santonin. T. H. P.

o-2′ : 4′-Dihydroxybenzoyltetrachlorobenzoic Acid and 2 : 3 : 4-Trichloro-6-hydroxyxanthone-1-carboxylic Acid and some of their Derivatives. W. R. Orndorff and W. A. Adamson (*J. Amer. Chem. Soc.*, 1918, **40**, 1235—1256).—After surveying the results of the numerous investigations on o-dihydroxybenzoylbenzoic acid (Baeyer's monoresorcinphthalein, *Annalen*, 1876, **183**, 23), the authors describe in detail the preparation of o-2′ : 4′-dihydroxybenzoyltetrachlorobenzoic acid from resorcinol and tetrachlorophthalic acid or its anhydride. Tetrachlorofluorescein is always formed, and some unchanged tetrachlorophthalic acid always remains, whatever the experimental conditions. The best results are obtained by heating resorcinol (4 parts) and tetrachlorophthalic acid (5 parts) for twelve to fifteen hours at a temperature not exceeding 131° (vapour of boiling xylene), whereby o-2′ : 4′-dihydroxybenzoyltetrachlorobenzoic acid is obtained in a yield of about 90%. The substance, after purification through its acetate, forms colourless crystals containing $2H_2O$, and has m. p. 227°, with decomposition into tetrachlorofluorescein and tetrachlorophthalic anhydride. It forms a *triacetate*, $C_{14}H_3O_5Cl_4Ac_3$, colourless crystals, m. p. 166—167°, a *sodium* salt,

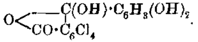
$$C_{14}H_5O_5Cl_4Na,2H_2O,$$

slightly grey crystals, m. p. about 295° (decomp.), *hydroxylammonium* salt, $C_{14}H_6O_5Cl_4.NH_2{\cdot}OH$, pale yellow crystals, m. p. 254° (decomp.; darkening at 230°), and with dry ammonia an unstable *triammonium* salt and a stable *monoammonium* salt. By bromination in glacial acetic acid, it yields o-3′ : 5′-*dibromo*-2′ : 4′-*dihydroxybenzoyltetrachlorobenzoic* acid, yellow needles, m. p. 211—212°, which at this temperature is converted into tetrachlorophthalic anhydride and tetrachloroeosin. The dibromo-acid forms a *triacetate*, colourless crystals, m. p. 204·5°, and an unstable, yellow *tetra-ammonium* salt, and a stable, less highly coloured *diammonium* salt.

By treatment for several hours with 5% alcoholic potassium hydroxide and subsequent acidification, the triacetate of the unbrominated acid yields 2 : 3 : 4-*trichloro*-6-*hydroxyxanthone*-1-*carboxylic acid*, colourless needles containing $2H_2O$, m. p. 279—280° (anhydrous). The same substance is obtained by boiling the dihydroxybenzoyltetrachlorobenzoic acid with 5% aqueous sodium hydroxide. It forms a *disodium* salt, $C_{14}H_3O_5Cl_3Na_2$, yellow

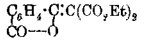
needles, *monoacetate*, colourless needles or prisms, decomp. 220—221°, and *ammonium* salt, $C_{14}H_4O_5Cl_3(NH_4)$.

The preceding results, particularly the fact that the triacetates are stable compounds which do not undergo any change when boiled with alcohol, are interpreted by ascribing to *o*-2′:4′-dihydroxybenzoyltetrachlorobenzoic acid the constitution

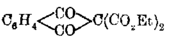


It seems highly probable from the results of this investigation that the formation of phthaleins takes place in two steps. First, an additive product of the phenol and the anhydride analogous to the preceding dihydroxy-acid is formed, and then this reacts with a second molecule of the phenol with the loss of water to form the phthalein. C. S.

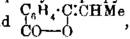
Constitution of Phthalyl- and Succinyl-malonic Esters. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1918, **51**, 1106—1115).—Two alternative formulæ for ethyl phthalylmalonate have been advocated, (I) by Wislicenus (A., 1888, 149) and (II) by Scheiber (A., 1912, i, 559):

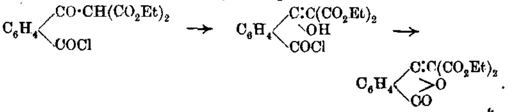


(I.)

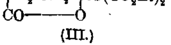


(II.)

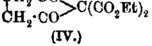
If formula II is correct, the ester should correspond in optical properties with indandiones, but this is not the case. A compound of the type I, on the other hand, should resemble ethyl benzylidenemalonate (A., 1911, ii, 782), when due allowance is made for the influence of the lactone ring. It is now found that these esters are optically related, like α-phenyl-Δ^{α}-propylene and ethylidenephthalide, CHPh:CHMe and , and consequently ethyl phthalylmalonate is correctly represented by formula I. This can be harmonised with the view that phthalyl chloride is symmetrical in structure, for the reaction with ethyl sodiomalonate can include stages which may be represented thus:



Similarly, ethyl succinylmalonate is abnormal in optical properties, and must therefore be expressed by formula III rather than by Scheiber's formula IV (A., 1909, i, 363):



(III.)



(IV.)

Ethyl phthalylmalonate (I) has m. p. 74 – 75°, $D_4^{84\cdot4}$ 1·1887, n_α 1·53416, n_D 1·54105, n_β 1·56155, at 84·4°; $E\Sigma_\alpha$ 2·13, $E\Sigma_D$ 2·25, $E\Sigma_\beta - \Sigma_\alpha$ 122%. 2 : 2-Diethylindan-1 : 3-dione (Freund and Fleischer, A., 1910, i. 490) has b. p. 157—159°/15 mm., $D_4^{14\cdot5}$ 1·0693, n_α 1·53658, n_D 1·54174, n_β 1·55632, n_γ 1·56967, at 14·5°, $E\Sigma_\alpha$ 1·43, $E\Sigma_D$ 1·49, $E\Sigma_\beta - \Sigma_\alpha$ 54%, $E\Sigma_\gamma - \Sigma_\alpha$ 57%. 4 : 7-Dimethyl-2 : 2-diethylindan-1 : 3-dione (Freund and Fleischer, A., 1916, i, 317) has b. p. 153°/12 mm., m. p. 51 – 52°, $D_4^{62\cdot4}$ 1·0174, n_α 1·52107, n_D 1·52598, n_β 1·54051, at 62·4°, $E\Sigma_\alpha$ 1·56, $E\Sigma_D$ 1·63, $E\Sigma_\beta - \Sigma_\alpha$ 63%. Ethyl succinylmalonate (III) has m. p. 68°, D_4^{73} 1·1675, n_α 1·46923, n_D 1·47245, n_β 1·48170, n_γ 1·48952, at 73°, $E\Sigma_\alpha$ 1·13, $E\Sigma_D$ 1·15, $E\Sigma_\beta - \Sigma_\alpha$ 41%, $E\Sigma_\gamma - \Sigma_\alpha$ 42%. Ethylidenephthalide has b. p. 152°/11 mm., m. p. 64°, $D_4^{99\cdot4}$ 1·1053, n_α 1·56394, n_D 1·57054, at 99·4, $E\Sigma_\alpha$ 2·29, $E\Sigma_D$ 2·36, and α-phenyl-Δ^α-propylene has $E\Sigma_\alpha$ 1·09, $E\Sigma_D$ 1·19. J. C. W.

***N*- and *O*-Methyl Ethers of Ketoximes. The Four Isomeric Methyl Ethers of Phenyl *p*-Tolyl Ketoxime.** LEOPOLD SEMPER and LEO LICHTENSTADT (*Ber.*, 1918, **51**, 928—942).—The *N*- and *O*-methyl ethers of ketoximes are produced in approximately equal quantities by the action of methyl sulphate on aqueous alcoholic alkaline solutions of the oximes. Thus, benzophenoneoxime yields the *N*-methyl ether, long needles, m. p. 102—103°, *hydrochloride*, m. p. 140—143°, and *O*-methyl ether, stout crystals, m. p. 60—61°. These are separated as follows: the initial product, after extraction with ether in the usual way, is triturated with light petroleum, b. p. 30—50°, which leaves most of the *N*-ether, this being recrystallised from a petroleum of b. p. 60—70°; the solution is treated with hydrogen chloride gas, which precipitates the remaining *N*-ether as hydrochloride, and then the *O*-ether is recovered by evaporation and crystallised from alcohol. The *N*-ether exhibits a tendency to form crystalline additive compounds, of which the following are some examples: with benzophenoneoxime, 1:1, cubes, m. p. 108—109° (compare Alessandri, A., 1915, i, 412); a *demihydrate*, transparent leaflets, m. p. 78—80°; a *compound* with quinol, 2:1, m. p. 186—186·5°; a *compound* with phenylcarbimide, 1:1, m. p. 141—142°. These are highly dissociated in solution. The *O*-ether forms no such compounds.

These preliminary experiments with a simple ketoxime paved the way for an attempt to isolate the two stereoisomeric pairs of ethers from an unsymmetrical ketoxime. For the purpose of investigation, phenyl *p*-tolyl ketone was chosen. A better method for isolating the α- and β-oximes of this has been devised (compare Hantzsch, A., 1890, 1273), and each isomeride converted into its *N*- and *O*-methyl ethers, making, therefore, the four possible isomerides.

The crude phenyl *p*-tolyl ketoxime is resolved into the two isomerides by crystallisation from 90% alcohol, which deposits most of the α-oxime on cooling, the β-oxime being recovered by adding to the hot mother liquor about three-fifths of its bulk of hot water, and cooling. The oximes are further purified by crystallisation

from pure alcohol. The α-oxime forms long, slender needles, m. p. 153—154°; the β-oxime crystallises in stout, transparent prisms, m. p. 136·5—137·5°. These are methylated as above, and the crude products treated in the same way. The two *N*-ethers have such tendencies to form additive compounds, however, that the products which are found to be sparingly soluble in the volatile petroleum are not the free ethers, but compounds with the unmethylated oximes. These are decomposed by dissolving them in dilute aqueous-alcoholic sodium hydroxide, precipitating the oxime by means of dilute sulphuric acid, and extracting the ethers after neutralisation of the filtrate. The *α-N-methyl ether* (I) forms colourless tablets, m. p. 91—92°, and yields the following *additive compounds*: with $0·5H_2O$, transparent, rhombic tablets, m. p. 66—67·5°; with α-phenyl *p*-tolyl ketoxime, needles, m. p. 106—107°; with the β-oxime, short prisms, m. p. 90—92°. The *α-O-methyl ether* (II) crystallises in needles, m. p. 64—68°.

$C_7H_7·CPh$	$C_7H_7·CPh$	$C_7H_7·CPh$	$C_7H_7·CPh$
Me·N:O	N·OMe	O:NMe	MeO·N
(I.)	(II.)	(III.)	(IV.)

The *β-N-methyl ether* (III) forms long, glistening prisms, m. p. 113—114°, and yields *additive compounds* with the β-oxime (stout prisms, m. p. 81—82°) and α-oxime (small cubes, m. p. 124—125°). The β-O-*methyl ether* (IV) has b. p. 184—185°/16 mm., 135—136°/0·5 mm. The two *N*-ethers are hydrolysed by boiling hydrochloric acid to phenyl *p*-tolyl ketone and β-methylhydroxylamine hydrochloride, and reduced by zinc dust and acetic acid to a base which may be isolated as a *hydrochloride*, $C_{15}H_{16}NCl$, m. p. 199—201°.

J. C. W.

Synthesis of some Phenolic Ketones. Taste of the Ketones. HIROSHI NOMURA and FUSATOSHI NOZAWA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, 79—92).—Vanillin and piperonal possess pleasant odours, whereas zingerone (methyl 4-hydroxy-3-methoxyphenylethyl-ketone) and the analogous 3:4-methylenedioxyphenylethyl methyl ketone have a pungent taste, but the intermediate products in the synthesis of these substances from vanillin and piperonal, namely, 4-hydroxy-3-methoxystyryl methyl ketone and 3:4-methylenedioxystyryl methyl ketone, are almost tasteless when first brought into contact with the tongue, although they gradually develop pungency. A number of compounds of similar constitution have now been examined with a view to discover the influence of constitutional variations on the taste. As in the above case of 4-hydroxy-3-methoxystyryl methyl ketone, the primary condensation product is generally less readily soluble than its final reduction product in organic solvents, and does not immediately taste pungent, whereas the reduction products are markedly pungent; styryl methyl ketone is exceptional in being readily soluble and having a very tingling taste. The presence of a free phenolic group is not essential to pungency, because phenylethyl methyl ketone, *p*-methoxyphenyl-

ethyl methyl ketone, and 3:4-methylenedioxyphenylethyl methyl ketone are all pungent. The degree of pungency, however, is greatly influenced by the position of the free hydroxyl group with respect to the ketonic side-chain; *o*-hydroxyphenylethyl methyl ketone in taste resembles 2-hydroxy-3-methoxyphenylethyl methyl ketone, and *p*-hydroxyphenylethyl methyl ketone resembles zingerone. As in these cases the hydroxyphenylethyl methyl ketones are less pungent than the corresponding hydroxymethoxyphenylethyl methyl ketones, the *m*-methoxyl group appears to increase the pungency. The influence of the simple hydrocarbon radicle attached to the ketonic group is not much greater than that of the position of the hydroxyl group, because phenyl 4-hydroxy-3-methoxyphenylethyl ketone has a pungent taste similar to zingerone.

Most of the compounds examined have been described earlier. m-*Hydroxyphenylethyl methyl ketone*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COMe$, m. p. 85—86°, was prepared through m-*hydroxystyryl methyl ketone*, needles, m. p. 97—98°, b. p. 208—209°/14 mm., from *m*-hydroxybenzaldehyde and acetone, the condensation of these substances being effected in a 10% solution of sodium hydroxide. p-*Hydroxyphenylethyl methyl ketone*, needles, m. p. 82—83°, was obtained by the catalytic reduction of *p*-hydroxystyryl methyl ketone in ethereal solution. The condensation of 2-hydroxy-3-methoxybenzaldehyde and acetone in alkaline solution yields 2-*hydroxy*-3-*methoxystyryl methyl ketone*,

$$OMe\cdot C_6H_3(OH)\cdot CH{:}CH\cdot COMe,$$

yellow crystals with $1H_2O$, m. p. 81—82°, or m. p. 77—77·5° if anhydrous, the catalytic reduction of which produces 2-*hydroxy*-3-*methoxyphenylethyl methyl ketone*, b. p. 206—207°/35 mm.; the pungent taste of this substance is accompanied by a paralysing effect, which is also observed with *o*-hydroxyphenylethyl methyl ketone. Vanillin and acetophenone undergo condensation in alkaline solution with the formation of *phenyl* 4-*hydroxy*-3-*methoxystyryl ketone*, $OMe\cdot C_6H_3(OH)\cdot CH{:}CH\cdot COPh$, yellow crystals, m. p. 92—93°, accompanied by *vanillylidenediacetophenone*,

$$OMe\cdot C_6H_3(OH)\cdot CH(CH_2\cdot COPh)_2,$$

colourless crystals, m. p. 131—132° (*benzoyl* derivative, colourless, m. p. 133°); on reduction in the usual way, phenyl 4-hydroxy-3-methoxystyryl ketone gave *phenyl* 4-*hydroxy*-3-*methoxyphenylethyl ketone*, $OMe\cdot C_6H_3(OH)\cdot CH_2\cdot CH_2\cdot COPh$, colourless scales, m. p. 97·5—98°. D. F. T.

Terpenes and Ethereal Oils. CXXII. Behaviour of the Nitrosochloride Additive Compounds towards Reagents which eliminate Hydrogen Chloride. O. WALLACH (*Annalen*, 1918, **414**, 257—270).—Sodium alkyloxides, anhydrous sodium acetate in glacial acetic acid, and dimethylaniline have been used to eliminate the elements of hydrogen chloride from nitrosochlorides, but each reagent has its disadvantages. The author now finds that an excellent conversion of a nitrosochloride into an oxime

is obtained by the use of a mixture of acetone and pyridine at not too high a temperature. Thus limonene nitrosochloride is converted into carvoxime by heating with acetone and pyridine for ten to fifteen minutes on the water-bath. In the case of certain nitrosochlorides, hydrogen chloride is eliminated in different ways by different reagents.

[With JOHANNA WOLFF.]—α-Terpineol nitrosochloride is converted into 8-hydroxy-Δ^6-menthene-2-oneoxime by heating with acetone and pyridine on the water-bath, but when heated with anhydrous sodium acetate and glacial acetic acid, it yields a crystalline substance, $C_{10}H_{17}O_2N$, m. p. 139°, which is saturated, yields the *keto-lactone of homoterpenylic acid* by *treatment with mineral acids*, and is identical with the substance obtained by Cusmano and Linari from the hydroxylamino-oxime (A., 1912, i, 272); it is regarded as the oxime-oxide.

$$CMe{<}{C(:NOH)\cdot CH_2 \atop CH_2 \text{———} CH_2}{>}CH\cdot CMe_2 .$$
$$\text{(CMe and CMe}_2\text{ linked through O)}$$

[With MARGARETE WALTER.]—β-Terpineol nitrosochloride does not yield a well-characterised product when treated with sodium methoxide (A., 1906, i, 372), and even when halogen acid is removed by the acetone-pyridine method, the expected hydroxy-oxime is only obtained by distillation in a vacuum as a slightly coloured, glassy mass.

The crystalline product, obtained by the prolonged action (about fourteen days) of 90% alcohol on β-terpineol nitrosochloride at the ordinary temperature and recrystallised from methyl alcohol, is not the hydroxy-oxime containing 1MeOH (Goodwin, *Diss.*, Göttingen, 1907), because it is a saturated substance, neither is it an oxime-oxide (see above), as is shown by the analytical data. Evidence is brought forward which indicates that the substance is a mixture, the halogen of the nitrosochloride being replaced partly by methoxyl, partly by ethoxyl, and partly by hydroxyl groups. Whether methyl or ethyl alcohol is used to decompose the nitrosochloride and for the recrystallisation of the product, the saturated, crystalline substances all yield the same compound after hydrolysis by sulphuric or oxalic acid, namely, the ketone, $C_{10}H_{14}O$ (semicarbazone, m. p. 218°), obtained by the hydrolysis by sulphuric acid of the unsaturated hydroxy-oxime resulting from the action of sodium methoxide (*loc. cit.*) or of pyridine on β-terpineol nitrosochloride. By reduction with sodium and alcohol, the ketone, which is also produced in bad yield by boiling the nitrosochloride with dilute sulphuric acid (1:4), yields an *alcohol*, $C_{10}H_{18}O$, b. p. 108—112°/20 mm. (*phenylurethane*, m. p. 144°). C. S.

Terpenes and Ethereal Oils. CXXIII. Behaviour of Dibrominated Hexacyclic Ketones in Relation to the Position of the Bromine Atoms. O. WALLACH (*Annalen*, 1918, **414**, 271—296).—The conversion of dibrominated *cyclo*hexanones into phenols is, of course, well known, and recently (A.,

1916, i, 213) unsaturated hydroaromatic tertiary alcohols have been converted into benzene hydrocarbons through the dibromo-additive compounds, but cases analogous to the smooth conversion of the 6-ring dibromopulegone into the 5-ring pulegenic acid under the action of alkali have hitherto not been known. The author has therefore examined the behaviour of a number of dibromo-derivatives of menthone and of carvomenthone when digested with 2% aqueous potassium hydroxide at the ordinary temperature for two to three days, and finds that the course of the reaction is determined essentially by the positions of the bromine atoms. The results may be generalised as follows: (1) Phenols are formed from dibromo-derivatives which have been obtained by the addition of bromine at an ethylenic linking adjacent to the carbonyl group and not separated from it by a substituent; for example, 1:2-dibromomenthone and 3:4-dibromocarvomenthone. The formation of the phenol does not always take place smoothly, comparatively stable monobromides sometimes being formed. (2) When the ethylenic linking is adjacent to the carbonyl group, but is separated from it by a substituent, the dibromo-derivative, for example, 4:5-dibromomenthone and 1:6-dibromocarvomenthone, readily undergoes fission of the ring with the production of an aliphatic ketonic acid with the same number of carbon atoms. (3) When the two bromine atoms are divided between the nucleus and the side-chains, or are both in the side-chains, the course of the reaction may be very varied and a general rule cannot be formulated. (4) Dibromo-derivatives in which the bromine atoms are attached to nuclear carbon atoms on either side of the carbonyl group, for example, 2:4-dibromomenthone and *1:3-dibromocarvomenthone*, are converted into pentacyclic hydroxycarboxylic acids (see following abstract).

[With H. E. Woodman.]—When shaken for three days with 2% aqueous potassium hydroxide, 8:9-dibromomenthan-2-one, prepared by the bromination of optically active dihydrocarvone, is converted, apart from small quantities of carvacrol and carvenone, into a heavy oil, which loses hydrogen bromide and yields carvacrol when distilled in a vacuum, and is reduced to dihydrocarvone by zinc and aqueous sodium hydroxide, and is therefore probably the *monobromide*, $CHBr:CMe\cdot CH<\begin{matrix}CH_2\cdot CH_2\\CH_2-CO\end{matrix}>CHMe$.

The crystalline dihydrocarvone dibromide, m. p. 69—70°, obtained by brominating *l*-dihydrocarvone in glacial acetic acid containing hydrogen bromide, is converted by 2% aqueous potassium hydroxide into an unsaturated *hydroxy-ketone*, $C_{10}H_{16}O_2$, b. p. 140°/16 mm., D^{20} 1·0285, n_D 1·4917 (*semicarbazone*, m. p. 123—124°), which yields carvacrol by warming with dilute sulphuric acid, and is possibly 8-hydroxy-Δ^6-menthen-2-one or 8-hydroxy-Δ^{8}-menthen-2-one.

3:4-Dibromocarvomenthone is converted by 2% aqueous potassium hydroxide into carvacrol, and, similarly, 1:2-dibromomenthone into *m-cresol*.

[With H. E. WOODMAN and W. JESSEN.]—1 : 6-Dibromocarvomenthone is converted by shaking with 2% aqueous potassium hydroxide for two to three hours at the ordinary temperature, and then for one to two hours at 100° into ε-keto-β-*iso*propylheptoic acid, which is identified as the optically active modification by the formation of the semicarbazone, m. p. 158—159°, and the oxime, m. p. 60—63° (rising to 87—89° by recrystallisation).

[With ADOLF HALLSTEIN.]—When 1 : 2-dibromomenthone is shaken for sixteen to twenty hours with the quantity of 2% aqueous potassium hydroxide calculated to remove all the bromine, a *monobromide*, $C_{10}H_{15}OBr$, m. p. 42—43°, is obtained, together with some thymol. The monobromide is converted into thymol by heating it alone, when hydrogen bromide is evolved, or with sodium methoxide. This behaviour and the method of preparation indicate that the monobromide is 2-bromo-Δ^{6}-menthen-3-one or 2-bromo-Δ^{1}-menthen-3-one, but the substance does not react readily with bromine, and yields by oxidation with alkaline potassium permanganate oxalic acid, volatile fatty acids, and a *ketonic acid*, $C_{10}H_{14}O_3$, m. p. 105—106° (*silver* salt, $C_{10}H_{13}O_3Ag$; *semicarbazone*, m. p. 225°); the formation of the last acid is not explicable by either of the formulæ given above.

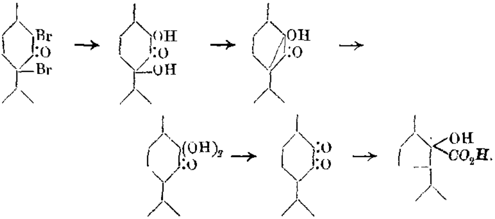
[With EMMA GROTE.]—4 : 5-Dibromomenthone is converted by 2% potassium hydroxide into an aliphatic *ketonic acid*, $C_{10}H_{18}O_3$ (*silver* salt, $C_{10}H_{17}O_3Ag$; *semicarbazone*, m. p. 161—163° [slowly heated] or 164—166° [rapidly heated]), which is probably *ε-keto-βζ-dimethyloctoic acid*, $COPr^{\beta}\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$.

An unsatisfactory attempt to prepare $\Delta^{4(5)}$-menthen-3-one from 4-bromomenthan-3-one is described. C. S.

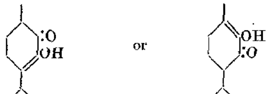
Terpenes and Ethereal Oils. CXXIV. Method of Transforming Hexacyclic Ketones into *cyclo*Pentanones Based on the Conversion of Dibrominated *cyclo*Hexanones into Pentacyclic α-Hydroxy-carboxylic Acids. O. WALLACH [with MATHILDE GERHARDT and WILHELM JESSEN] (*Annalen*, 1918, **414**, 296—366).—A portion of the work has already appeared (A., 1916, i, 487).

The dibrominated *cyclo*hexanones which contain the bromine atoms in such positions that pentacyclic α-hydroxy-carboxylic acids are produced by the action of alkalis (see preceding abstract) are in general easily obtained by treating the *cyclo*hexanone in glacial acetic acid solution with four atoms of bromine. Since *cyclo*pentanones are known only in small number, whilst *cyclo*hexanones can be obtained in large numbers, not only from natural sources, but also from phenols by Sabatier's method and by Knoevenagel's synthesis, it is of importance to find out whether it is possible quite generally to convert *cyclo*hexanones into pentacyclic α-hydroxy-carboxylic acids with the same number of carbon atoms, from which *cyclo*pentanones can be obtained by oxidation. Up to the present time, nine *cyclo*hexanones have been converted into *cyclo*pentanones by the elimination of a nuclear methylene group, the penta-

cyclic α-hydroxy-carboxylic acids being intermediate products. The formation of these would be easily explicable if the original dibromo*cyclo*hexanone contained a CBr_2 group adjacent to the carbonyl group, because the alkali would then produce an ortho-diketone, from which the pentacyclic α-hydroxy-carboxylic acid would be formed by a benzilic acid transformation. This simple explanation is inapplicable, for two reasons: (1) It is proved quite definitely that by direct substitution in menthone and carvomenthone, the two bromine atoms are not attached to one and the same carbon atom, but that one bromine atom replaces the tertiary hydrogen atom adjacent to the carbonyl group and the other enters the methylene group on the other side of the carbonyl group. (2) Although compounds having the composition of *o*-diketones can be isolated, they do not exhibit the properties of such substances, but behave as unsaturated ketols. Such compounds derived from the dibromomenthone and the dibromocarvomenthone are identical and yield the same pentacyclic hydroxy-carboxylic acid. The author's explanation is represented schematically: for dibromomenthone,



and similarly for the dibromocarvomenthone; the same *o*-diketone is formed in both cases, but when isolated isomerises to the unsaturated ketol,



The bromination of 1:3-dimethyl*cyclo*hexan-5-one in cold glacial acetic acid produces two dibromo-compounds, an *α-dibromide*, $C_8H_{12}OBr_2$, needles, m. p. 163—164° (decomp.), which is scarcely attacked by alkali, and an isomeric *β-dibromide*, prisms, m. p. 60—61°, which is converted by 2% aqueous potassium hydroxide into the *ketol*, $C_8H_{12}O_2$, m. p. 71—72°. The ketol, which is removed from the acidified liquid by steam, is converted by con-

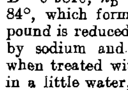
centrated aqueous potassium hydroxide at 140° into *4-hydroxy-1:3-dimethyl*cyclo*pentane-4-carboxylic acid*, $C_8H_{14}O_3$, colourless crystals, m. p. 92—93°, which yields *1:3-dimethyl*cyclo*pentan-4-one*, b. p. 152—154°, D^{17} 0·8950, n_D^{17} 1·4330 (*semicarbazone*, m. p. 165—166°), by warming with lead peroxide and sulphuric acid. C. S.

Terpenes and Ethereal Oils. CXXV. Compounds of the Eucarvone Series. O. WALLACH [with MAX STANDACHER]. (*Annalen*, 1918, **414**, 367—375).—Assuming the constitution given to β-dihydroeucarvoxime (*Annalen*, 1914, **403**, 87) to be correct, the reduction of the substance should yield tetrahydroeucarvylamine. This is found to be so. When reduced by sodium and alcohol, the oxime is converted into a *base*, $C_{10}H_{19}\cdot NH_2$, b. p. 208·5°, D^{21} 0·8680, n_D 1·4665, which forms a *carbamide*, m. p. 139°, *phenylcarbamide*, m. p. 143—146°, *trimethylammonium iodide*, m. p. about 200°, and an *acetyl* derivative, m. p. 110·5°, the last being identical with the substance obtained by acetylating the base prepared by the reduction of tetrahydroeucarvoxime.

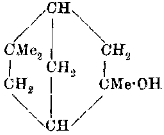
By *bromination in glacial acetic acid at 0°, tetrahydroeucarvone* yields a *monobromo*-derivative, $C_{10}H_{17}OBr$, crystals, m. p. 32°, which is converted by 3% aqueous potassium hydroxide into *hydroxytetrahydroeucarvone*, $OH\cdot C_{10}H_{17}O$, b. p. 98°/12·5 mm., D^{20} 0·9810, n_D 1·4626 (*semicarbazone*, m. p. 193°; *oxime*, m. p. 84°, which forms a crystalline *sodium* salt). The hydroxy-compound is reduced to a *glycol*, $C_{10}H_{18}(OH)_2$, b. p. 112—117°/4 mm., by sodium and alcohol, and yields a *chromate*, $(C_{10}H_{17}O)_2CrO_4$, when treated with sulphuric acid and chromium trioxide dissolved in a little water, at a temperature not exceeding 0°.

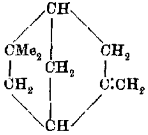
When treated with bromine (2 mols.) in glacial acetic acid without cooling, tetrahydroeucarvone yields *dibromotetrahydroeucarvone*, $C_{10}H_{16}OBr_2$, colourless prisms, m. p. 68°, which is converted by 4% aqueous potassium hydroxide at 100° into an *acid*, $C_{10}H_{16}O_2$, crystals, m. p. 91·5—92·5° (*silver* salt, $C_{10}H_{15}O_2Ag$). The acid is saturated, odourless, and somewhat easily volatile with steam; its constitution has not yet been determined. When treated with methyl-alcoholic sodium methoxide, dibromotetrahydroeucarvone yields a *substance*, $C_{10}H_{16}O_2$, b. p. 218—219°, D^{20} 0·979, n_D 1·4698, isomeric with the preceding acid, the nature of which has not yet been ascertained. C. S.

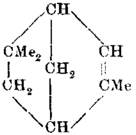
Isomerisation Product of Carvone in the Light. Carvonecamphor. II. E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 238—242. Compare A., 1915, i, 425).—When the oxime of carvonecamphor is heated with 20% sulphuric acid on the water-bath, *iso*carvonecamphor is obtained, the yield being almost theoretical. Phosphorus pentachloride reacts with the oxime in chloroform solution, giving 2-chlorocymene. From these and other reactions previously described, the annexed constitution is suggested for carvonecamphor. R. V. S.

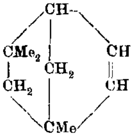


The Partial Synthesis of β- and γ-Fenchene. GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennicae*, 1917, *A*, [x], **15**, 1—15; from *Chem. Zentr.*, 1918, i, 622. Compare A., 1917, i, 398, 466).—In extension of the earlier conversion of *dl*-α-fenchocamphorone into α-fenchene, the authors have treated *dl*-β-fenchocamphorone with magnesium methyl iodide, with production of *methyl-β-fenchocamphorol* (annexed formula, I), prisms, m. p.


(I.)


(II.)


(III.)


(IV.)

66—67°, b. p. 77°/9 mm., 85°/15 mm.; *phenylurethane* derivative, $C_{17}H_{23}O_2N$, obtained by the action of phenylcarbimide, needles, m. p. 133·5—134°; *acetyl* derivative, $C_{12}H_{20}O_2$, b. p. 212·5°/766 mm., 80·5—81°/8 mm., D_4^{20} 0·9769, n_D^{20} 1·45884. When heated with potassium hydrogen sulphate, methyl-β-fenchocamphorol yields a mixture of hydrocarbons consisting mainly of dl-β-*fenchene* (formula II), b. p. 151—153°, D_4^{20} 0·8596, n_D^{20} 1·46581, with an endocyclic γ-fenchene (formula III), b. p. 146—148°, D_4^{20} 0·8539 n_D^{20} 1·46063, identical with the product of the interaction of *dl*-fenchyl alcohol and potassium hydrogen sulphate; *dl*-β-fenchene on oxidation with potassium permanganate gives dl-*hydroxy-β-fenchenic* acid, needles, m. p. 124—125° (*acetyl* derivative, $C_{12}H_{18}O_4$, scales, m. p. 117—118°); the acid is oxidised by lead dioxide and sulphuric acid to *dl*-β-fenchocamphorone, and this further by potassium permanganate to *apo*fenchocamphoric acid. The endocyclic fenchene (formula IV) described earlier (Roschier, *Diss.*, Helsinki, 1917), and termed *isoallo*fenchene by Semmler and *iso*fenchylene by Qvist, should be designated δ- or *iso*-fenchene. The compound now described by the authors as β-fenchene has been earlier termed *iso*fenchene by Semmler and *Dd*- (or *Ll*-) fenchene by Wallach. D. F. T.

Terpenes and Ethereal Oils. CXX. O. WALLACH (*Annalen*, 1917, **414**, 195—233).—Most of the work has been already published (A., 1916, i, 213). The following is new.

[With KURT PELIKAN.]—From the accepted *formulæ* of pinol hydrate and dihydrocarveol, the expectation is justifiable that the reduction product of the former will be identical with the menthane-2:8-diol obtained from the latter by the addition of water (Wallach, *Annalen*, 1911, **380**, 161). The expectation, however, is not fulfilled. *i*-Pinol hydrate yields by reduction a glycol, dihydropinol hydrate, m. p. 139—141°, whilst the *i*-glycol obtained from dihydrocarveol has m. p. 108—109°. Also, *d*-pinol hydrate (sobrerol) reduced in methyl-alcoholic solution by Paal's method yields a *glycol*, $C_{10}H_{18}(OH)_2$, m. p. 158—159°, $[\alpha]_D^{20°}$ −40°26′ in alcohol, whilst the glycol derived from the optically active dihydrocarveol has m. p. 113—114°.

The behaviour of pinol hydrate on reduction, therefore, has been examined. When it is reduced by hydrogen and colloidal palladium in the absence of free acid, there occurs, in addition to the normal reduction, a by-reaction in which the pinol hydrate is dehydrated and the resulting unsaturated monohydric alcohol is reduced to tetrahydrocarveol. This result not only again shows that unsaturated glycols are not always smoothly reduced to the saturated glycols in the presence of colloidal metal (compare A., 1912, i, 878), but is also a further proof that in pinol hydrate a hydroxyl group occurs in position 2.

i- or *l*-Dihydropinol hydrate is converted into terpinene dihydrobromide by treatment with hydrogen bromide in glacial acetic acid. A similar transformation is not produced by hydrogen chloride. Moreover, the menthane-2:8-diol obtained from dihydrocarveol does not behave in this way.

It is shown that dihydropinol hydrate is not identical with menthane-1:4-diol or with *menthane*-2:4-*diol*, obtained by reducing sabinene glycol by Paal's method. The latter diol has b. p. 135—140°/9 mm.; the distillate solidifies completely (m. p. 93—94°), but separates as an oil from solvents on account of its great solubility. When dehydrated by oxalic acid and water, it yields a small quantity of a hydrocarbon, b. p. 172—182°, D^{20} 0·866, showing the reactions of terpinene, the main product being an unsaturated *alcohol*, $C_{10}H_{17}\cdot OH$, b. p. 219—221°, D^{22} 0·9250, n_D 1·4790, which yields carvenone by oxidation with chromic acid and tetrahydrocarveol by reduction by Paal's method. The alcohol would therefore appear to be Δ^3-*menthene*-2-*ol*, but that $\Delta^{4(8)}$-menthene-2-ol is also present is indicated by the formation of acetone when the alcohol is oxidised by potassium permanganate. When *i*-dihydropinol hydrate is warmed with oxalic acid and water, the main product is a saturated *oxide* having an odour of cineole; dihydrocarveol is formed as a by-product. C. S.

The Pungent Principles of Ginger. II. HIROSHI NOMURA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, 67—77. Compare T., 1917, **111**, 769).—By distillation of the pungent principles of Japanese ginger under reduced pressure, the author has been able to isolate,

in addition to zingerone, a substance, *shogaol*, $C_{17}H_{24}O_3$, b. p. 175—185°/0·4—0·5 mm., 231—238°/15·5 mm., M.W. in benzene 262, D_4^{25} 1·0448, n_D^{25} 1·52467; this substance is phenolic (*acetyl* derivative, b. p. 183—188°/0·6 mm.; *methyl* ether, b. p. 160—165°/0·06 mm.; *ethyl* ether, b. p. 181—186°/0·65 mm.), and also contains a methoxy-group; the third oxygen atom is probably ketonic. Oxidation of the ethyl ether with alkaline permanganate yields ethylvanillic acid, so that the constitution of shogaol may be represented $OH{\cdot}C{<}^{C(OMe){:}CH}_{CH\text{——}CH}{>}C{\cdot}C_{10}H_{17}O$. From the facts that on reduction in ethereal solution with hydrogen and platinum-black shogaol yields *dihydroshogaol*, $C_{17}H_{26}O_3$, b. p. 166—169°/0·15 mm., and that the molecular refraction of shogaol greatly exceeds the calculated value, it appears probable that shogaol is a β-unsaturated ketone. D. F. T.

Some Derivatives of the Pyrryl Methyl Ketones with Furfuraldehyde. C. FINZI and E. VECCHI (*Gazzetta*, 1917, **47**, ii, 10—19).—Whereas benzaldehyde reacts equally easily with the 2- and 3-acetyl derivatives of pyrrole, the results now described show that furfuraldehyde reacts well and almost quantitatively with acetyl groups in the 2-position, but that the reaction with a 3-acetyl group appears to be influenced by the presence of some substituent group in the pyrrole nucleus. In view of their analogy to cinnamyl derivatives, the compounds obtained by the condensation of furfuraldehyde with the acetylpyrroles are termed *furacryl* derivatives.

The *compound*, $\overset{CH\cdot CH}{\underset{CH\cdot NH}{\|}}{>}C{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O$, obtained by the interaction of 2-acetylpyrrole and furfuraldehyde, forms slightly iridescent, yellow needles, m. p. 134—135°.

The *compound*, $\overset{CH\cdot CMe}{\underset{CMe\cdot NH}{\|}}{>}C{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O$, obtained from 2-acetyl-3:5-dimethylpyrrole and furfuraldehyde, forms sulphur-yellow needles, m. p. 181—182°.

The *compound*, $C_4HNMe_2(CO_2Et){\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O$, formed from ethyl 2-acetyl-3:5-dimethylpyrrole-4-carboxylate and furfuraldehyde, crystallises in lemon-yellow, prismatic needles, m. p. 184—185°. The corresponding *acid*,

$$C_4HNMe_2(CO_2H){\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O,$$

obtained either by hydrolysing this ester or by starting from the pyrrolecarboxylic acid, forms minute, yellow, prismatic crystals, m. p. 287—288°; the insoluble *silver* salt was analysed.

The *compound*, $\overset{CO_2Et\cdot C{=\!=}CMe}{\underset{NH\cdot CMe}{|}}{>}C{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O$, obtained from ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate and furfuraldehyde, forms sulphur-yellow needles, m. p. 149—150°. The corresponding *acid* forms minute, straw-yellow, prismatic needles, m. p. 179—180° (decomp.); the corresponding *silver* salt was analysed.

The *compound*, $\begin{matrix}CH:C(CO\cdot CH:CH\cdot C_4H_3O)\\ CH:C(CO\cdot CH:CH\cdot C_4H_3O)\end{matrix}>NH$, obtained from 2:5-diacetylpyrrole and furfuraldehyde, forms lemon-yellow crystals, m. p. 238—240°, and dissolves in concentrated sulphuric acid in the cold, giving an intense blue coloration with a violet border; dilution of this solution results in the precipitation of the unaltered compound. The corresponding dicinnamyl derivative is very slightly soluble in cold concentrated sulphuric acid, and only in the hot dissolves somewhat, giving a reddish-violet coloration.

The *compound*, $\begin{matrix}CAc\cdot CMe\\ \| \\ CMe\cdot NH\end{matrix}>C\cdot CO\cdot CH:CH\cdot C_4H_3O$, formed from 2:4-diacetyl-3:5-dimethylpyrrole and furfuraldehyde, crystallises in tufts of prismatic needles, m. p. 170°, and dissolves in concentrated sulphuric acid, giving a carmine coloration, changing later to amaranth; on dilution, this solution deposits the original compound. The corresponding dicinnamyl derivative dissolves only slightly and slowly in cold concentrated sulphuric acid, giving the orange-yellow coloration shown with all the furacryl and cinnamyl derivatives of the pyrroles as yet examined. T. H. P.

New Synthesis of Tetraphenylpyrrole. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1918, **113**, 639—645).—Adopting a hypothesis, represented by the following scheme, to account for the conversion of phenylhydrazones into indoles,

$$NHPh\cdot N:CMe_2 \longrightarrow NHPh\cdot NH\cdot CMe:CH_2 \longrightarrow$$
$$NH_2\cdot C_6H_4\cdot CH:CMe\cdot NH_2,HCl \longrightarrow C_6H_4<\begin{matrix}CH\\ NH\end{matrix}>CMe + NH_4Cl,$$

the authors record the process of reasoning which led them to expect that azines of substances containing the group $\cdot CH_2\cdot CO\cdot$ would, under correct conditions, be transformed into pyrroles. Their expectation was fulfilled in the case of phenylbenzylketazine, which yielded tetraphenylpyrrole and ammonium chloride when heated at 180° in a current of dry hydrogen chloride. The simple aliphatic azines, such as acetaldazine and dimethylketazine, yield the corresponding pyrazoles and pyrazolines.

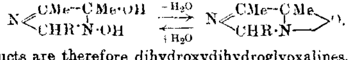
Ketazines are obtained in excellent yield by heating the ketone with the calculated quantity of hydrazine sulphate in boiling aqueous alcohol in the presence of an excess of sodium acetate.

C. S.

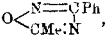
Course of the Reaction between Diacetyl [Dimethyl Diketone] Monoxime and Aldehydes in the Presence of Ammonia. Formation of Dihydroxydihydroglyoxalines. OTTO DIELS (*Ber.*, 1918, **51**, 965—976).—The author has already shown that when dimethyl diketone monoxime is condensed with aldehydes in the presence of a concentrated alkali hydroxide, oximes of unsaturated $\alpha\beta$-diketones are formed, thus: $R\cdot CHO + COMe\cdot CMe:N\cdot OH = H_2O + R\cdot CH:CH\cdot CAc:N\cdot OH$ (A., 1913, i, 875), whereas *compounds of the type* $RC<\begin{matrix}O\ CMe\\ N\cdot CMe\end{matrix}>O$ are produced if

concentrated hydrochloric acid is the condensing agent (A., 1915, i, 690). It is now found that a reaction also takes place in the presence of aqueous-alcoholic ammonia, the products being characterised by the fact that they readily lose water on warming and combine with it again most easily. As ammonia takes part in the reaction, it is assumed that the aldehydes condense with the oxime in the form of their ammonia compounds, and the process is *indicated in the following way:*

$NH_2 \cdot CHR \cdot OH + COMe \cdot CMe{:}N \cdot OH \longrightarrow$



The products are therefore dihydroxydihydroglyoxalines.

For example, benzaldehyde yields the *compound*, $C_{11}H_{14}O_2N_2$, which crystallises in compact needles, forms colourless, crystalline salts with sodium hydroxide or nitric and sulphuric acids, and melts at 120—121° with evolution of water, thereby changing into the *compound*, $C_{11}H_{12}ON_2$, m. p. 180°. On oxidation with dilute chromic acid, it yields acetic and benzoic acids and 3-*phenyl*-5-*methyl*-1 : 2 : 4-*oxadiazole*, , which has m. p. 41°, b. p. 252—253°/763 mm., and the odour of methyl salicylate, and is the "*benzenylazoximethenyl*" *described by Tiemann and Krüger* (A., 1884, 1326). On reduction with zinc dust and 50% acetic acid, it forms a *base*, $C_{11}H_{14}N_2$, which has m. p. 242°, sublimes readily, and gives well-defined salts with the mineral acids.

Furfuraldehyde reacts at about 40—60° to give the *compound*, $C_9H_{12}O_3N_2$, which crystallises from hot water in prisms, forms a crystalline hydrochloride and sulphate, dissolves in dilute alkali hydroxides, gives a pale amethyst solution in concentrated sulphuric acid which is changed to emerald-green on adding a trace of nitric acid, melts at 112—113°, losing water and changing into the *compound*, $C_9H_{10}O_2N_2$, m. p. 170—171°. At 0°, the product is hydrofurfuramide, which does not react further with dimethyl diketone monoxime unless the mixture is warmed with a little free ammonia.

Cinnamaldehyde forms the *compound*, $C_{13}H_{16}O_2N_2$, which crystallises in glistening, pale yellow prisms, m. p. 138—139° (*decomp.*), and gives very sparingly soluble salts with the mineral acids.

Acetaldehyde-ammonia and dimethyl diketone monoxime yield the *compound*, $C_{10}H_{17}O_3N_3$, in large crystals, m. p. 129—130°. This seems to be loosely compounded of one molecule of the oxime and the expected *compound*, $C_6H_{12}O_2N_2$, analogous to the above (R = Me), which crystallises in druses, m. p. 80—81°, and loses water to form the *compound*, $C_6H_{10}ON_2$, m. p. 134°, for resolution into these two products can be effected by warming with water, alkalis, acids, or phenylhydrazine. J. C. W.

Nature of Cyclic Quinoneimide Dyes. F. KEHRMANN (*Annalen*, 1917, **414**, 131—188).—A theoretical paper containing a discussion of the results of investigations of the constitutions of

cyclic quinoneimine dyes. The classes discussed are azonium compounds (azines, safranines, indulines), azthionium (thionines), azoxonium (azoxines), carboxonium and carbothionium (pyronines, rosamines, thiopyronines, cyanopyronines, cyanoacridines), and acridonium. The discussion starts with the desmotropy of 6-hydroxynaphthaphenazine recorded by Kehrmann and Messinger in 1891, and this strikes the key-note of the author's treatment of the subject. The dyes are in general regarded as desmotropic substances which acquire the ortho- or the para-quinonoid structure according to the conditions; for example, rosinduline and induline salts are orthoquinonoid, but the free bases are paraquinonoid.

C. S.

Constitution of Pyronine. J. VON BRAUN (*Ber.*, 1918, **51**, 440—441).—*Polemical*, replying to Kehrmann's references (preceding abstract) to the author's views (A., 1916, i, 663).

J. C. W.

Acylated *p*-Phenylenemethyldiamines. GILBERT T. MORGAN and WILLIAM ROBINSON GRIST (T., 1918, **113**, 688—694).—Acyl derivatives of *p*-phenylenediamine are of technical importance for the production of bisazo-dyes. The following intermediates have been prepared from methylaniline: p-*nitromethylformanilide*, $NO_2\cdot C_6H_4\cdot NMe\cdot CHO$, pale yellow prisms, m. p. 118—120°; p-*aminomethylformanilide* (as-*formyl*-p-*phenylenemethyldiamine*), colourless needles, m. p. 132°; the corresponding *acetanilide*, colourless needles, m. p. 63°. The last two substances by treatment with nitrous anhydride in dry acetone at −10° yield *formylmethylaminobenzene-4-diazohydroxide*, $CHO\cdot NMe\cdot C_6H_4\cdot N_2\cdot OH$, greyish-white granules, decomp. 131—132°, and the corresponding *acetyl* compound, decomp. 131—132°, respectively, which react with dry β-naphthol to form *formylmethylaminobenzene-4-azo-β-naphthol*, ill-defined crystals, m. p. 160—161°, and the corresponding *acetyl* compound, red tablets or flattened needles, m. p. 139°; the two azo-β-naphthols were also obtained by coupling the diazotised *p*-aminomethylacylanilides with β-naphthol in alkaline solution.

C. S.

Preparation of 4-Diallylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.-P., 304983; from *Chem. Zentr.*, 1918, i, 789).—4-Diallylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, colourless crystals, m. p. 90°, possessing antipyretic and narcotic effect, is obtainable by the action of allyl haloids on 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone in the warm, preferably in the presence of a solvent or diluent, and with the addition of some substance to remove the acid produced.

D. F. T.

Theory of Ring Closure. RICHARD MEYER and HERMANN LÜDERS (*Annalen*, 1918, **415**, 29—50).—Since Thiele and Falk (A., 1906, i, 750) have shown that Anderlini's so-called *o*-phenylene-

phthalamide, prepared from *o*-phenylenediamine and phthalic acid (A., 1894, i, 375), is really 2-carboxyphenylbenziminazole, the authors have reinvestigated the action of *o*-phenylenediamine with succinic acid, and find that two compounds only are formed, not three as stated previously (A., 1903, i, 442; 1906, i, 765), the substance, m. p. 236°, supposed to be the 8-ring *o*-phenylenesuccinamide being identical with benziminazole-2-propionic acid. It yields a *methyl* ester, quadratic leaflets, m. p. 144—145°, *ethyl* ester, needles, m. p. 135—136°, and *amide*, prismatic needles, m. p. 254° (decomp.); the *silver* salt, small prisms, *copper* salt, blue plates, and *platinichloride*, yellow crystals, are described, and also the *platinichloride* of the methyl ester. By heating at 230—240°, it loses water and yields 1:2-*propionylenebenziminazole*,

$$\begin{array}{l} N{=\!=}C\cdot CH_2 \\ C_6H_4\cdot N{-}CO \end{array}\!\!>\!CH_2,$$

colourless needles, m. p. 171°.

Since, therefore, the compounds obtained from *o*-phenylenediamine and phthalic acid and succinic acid respectively are 5-ring, not 8-ring compounds, the behaviour of the diamine with other dibasic acids (Meyer, *loc. cit.*) requires reinvestigation. Cox (*Diss.*, Strassburg, 1908) has already shown that the product from the diamine and malonic acid is easily split into its generators, does not contain a carboxyl group, and is the 7-ring *o*-phenylenemalonamide, as stated by Meyer. It is now shown that the product from *o*-phenylenediamine and ethyl *iso*succinate behaves similarly, and is, as stated previously (*loc. cit.*), the 7-ring *o*-phenylene*iso*succinamide, although its infusibility and sparing solubility suggest that the molecule is polymerised.

The reactivity of the methine hydrogen atom in ethyl *iso*succinate has been investigated. No reaction occurs with formaldehyde or benzaldehyde, and the sodio-derivative of the ester does not yield condensation products with succinyl chloride or phthalyl chloride, but reacts with benzoyl chloride and with cinnamoyl chloride in dry ether to form *ethyl a-benzoyl*isosuccinate, $CMeBz(CO_2Et)_2$, small, quadratic plates, m. p. 36—38°, b. p. 193—195°/18 mm., and *ethyl a-cinnamoyl*isosuccinate, a pale yellow, viscous liquid, b. p. 225—230°/15 mm., respectively. *iso*Succinic acid and benzoic or cinnamic acid are obtained when attempts are made to hydrolyse these esters, and the reaction with phenylhydrazine results in the formation of benzoyl- or cinnamoyl-phenylhydrazine and ethyl *iso*succinate.

When heated slowly, *m*-nitrophthalanilic acid apparently has m. p. 240° (Meyer, *loc. cit.*), but when heated rapidly it melts at 202° with violent foaming (Tingle and Rolker, A., 1909, i, 28), resolidifies, and melts again at 240°. This phenomenon is due to the conversion of the anilic acid into the anil, which has m. p. 240—242°. The anilic acid crystallises in colourless needles, not faintly yellow, as previously stated (Meyer, *loc. cit.*). The fusion of *p*-nitrophthalanilic acid is similar; at 190—192° fusion occurs

with violent foaming, and the product resolidifies and melts again at 260°, the m. p. of the anil. *o*-Nitrophthalanilic acid, yellow leaflets, has m. p. 146—148° (without decomp.), but at 190—200° it loses water and yields the anil, colourless needles, m. p. 200—201°. *m*-Nitrosuccinanilic acid has m. p. 179° (stated previously, 181—182°, *loc. cit.*), and the anil has m. p. 174°.

C. S.

Action of Ortho- and of Peri-diamines, and of Ethylenediamine, on γ-Lactones. A. Bistrzycki and Walther Schmutz (*Annalen*, 1918, **416**, 1—28).—The behaviour of *o*-phenylenediamine and of 1:8-naphthylenediamine with lactones derived from certain alcohol-acids has been examined; two molecules of water are eliminated and benziminazole derivatives produced. When lactones derived from phenolic acids are employed, benziminazole derivatives are again obtained, but the condensation does not proceed beyond the elimination of one molecule of water. Thus phthalide and *o*-phenylenediamine hydrochloride, heated at from about 180° to 200°, yield the hydrochloride of *o*-benzylenebenziminazole, m. p. 212—213° (Thiele and Falk, A., 1906, i, 751, give 210°) (*picrate*, yellow needles, decomp. 243·5°), whilst phthalide and 1:8-naphthylenediamine in a similar reaction yield the hydrochloride of benzyleneperimidine (phthaloperine). Whilst phthalophenone does not react with *o*-phenylenediamine (or its hydrochloride) or with *p*-ethoxy-*o*-phenylenediamine, phenolphthalein reacts extremely vigorously with the former at 230°, yielding *di*-p-*hydroxyphenylbenzylenebenziminazole*, $\begin{array}{l} C(C_6H_4\cdot OH)_2\cdot N\cdot C_6H_4 \\ C_6H_4 \text{———} C:N \end{array}$, needles, decomp. 354—355°, which gives a colourless solution in dilute aqueous potassium hydroxide, and forms a *picrate*, stout prisms, m. p. 203—204°, and *diacetate*, best isolated in the form of the *picrate*, $C_{36}H_{25}O_{11}N_5$, yellow needles, decomp. 285·5—286°. When a mixture of valerolactone and *o*-phenylenediamine is heated, finally at 270°, 1:2-(1′-*methyltrimethylene*)-*benziminazole*,

$$CH_2{<}\begin{array}{l} CHMe\cdot N\cdot C_6H_4 \\ CH_2 \text{—} C:N \end{array}$$

is obtained in bad yield as a brown oil; the *picrate*, yellow, microscopic prisms, has m. p. 222—224° (darkening).

o-Phenylenediamine and the lactone of *o*-hydroxydiphenylacetic acid react quantitatively at 120—130° to give 2-o-*hydroxybenzhydrylbenziminazole*, $C_6H_4{<}{}^{\text{—N—}}_{NH}{>}C\cdot CHPh\cdot C_6H_4\cdot OH$, m. p. 246—247°, which separates from ethyl alcohol or benzene in microscopic, colourless leaflets containing 1 mol. of solvent, and forms a *picrate*, stout, yellow prisms, m. p. 216°, with previous darkening; attempts to eliminate a second molecule of water by fusion with phosphoric oxide or zinc chloride were unsuccessful. The same lactone reacts with *p*-ethoxy-*o*-phenylenediamine to form

4(or 3)-*ethoxy-2-o-hydroxybenzhydrylbenziminazole*,
$C_{22}H_{20}O_2N_2,H_2O$,
colourless prisms, m. p. 110—120°, with loss of the water of crystallisation, with 1 : 8-naphthylenediamine at 70—100° to form 2-*o-hydroxybenzhydrylperimidine*, $C_{10}H_6<\substack{-N=\\NH}>C\cdot CHPh\cdot C_6H_4\cdot OH$, colourless, microscopic plates, m. p. 295—297° (decomp.), and with 1:2-naphthylenediamine at 120—140° quantitatively to form 2-*o-hydroxybenzhydrylnaphthiminazole*, $C_{24}H_{18}ON_2$, colourless, microscopic prisms, m. p. 294—295°, in which it has not been determined whether the NH-group is attached to the naphthalene nucleus in the α- or the β-position. The lactone of 2-hydroxy-5-methyltriphenylacetic acid does not react with phenylenediamine or its hydrochloride.

The behaviour of ethylenediamine with lactones is quite different from that of aromatic diamines. When phthalide (2 mols.) dissolved in absolute alcohol is boiled with a 50% aqueous solution of ethylenediamine (1 or 2 mols.), an additive compound, NN′-*ethylenebis-(2-hydroxymethylbenzamide)*,
$C_2H_4(NH\cdot CO\cdot C_6H_4\cdot CH_2\cdot OH)_2$,
colourless needles, m. p. 183·5°, is obtained on cooling after pouring into water, which forms a *diphenylurethane*, $C_{32}H_{30}O_6N_4$, colourless needles, decomp. 190° (rapidly heated), when heated with phenylcarbimide at 160°, and is oxidised by chromic and glacial acetic acids to the dicarboxylic acid, which immediately changes to diphthalylethylenedi-imide by loss of water. The additive compound loses water above its m. p. and undergoes a partial change into NN′-*ethylenediphthalimidine*,

$$C_2H_4\left(N<\substack{CH_2\\CO}>C_6H_4\right)_2,$$

colourless prisms or needles, m. p. 227·5—229°, which is also obtained in 80—90% yield by heating phthalide (2 mols.) and ethylenediamine (1 mol.) at 300° for three hours. Ethylenediphthalimidine is quite stable to boiling aqueous or alcoholic potassium hydroxide. By treatment with boiling chromic and pure acetic acids, it can be oxidised successively to NN′-*ethylenephthalimidephthalimidine*,

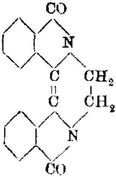
$$C_6H_4<\substack{CH_2\\CO}>N\cdot CH_2\cdot CH_2\cdot N<\substack{CO\\CO}>C_6H_4,$$

colourless needles, m. p. 190—191°, and to NN′-ethylenediphthalimide (diphthalylethylenedi-imide, Anderlini, A., 1894, i, 490). The former of these is hydrolysed by hot, moderately dilute aqueous potassium hydroxide to NN′-*ethylenephthalimidine*-o-*carboxybenzamide*, $C_6H_4<\substack{CH_2\\CO}>N\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, colourless prisms, decomp. 172—173° (*silver* salt, $C_{18}H_{15}O_4N_2Ag$, tufts of needles).

When treated with bromine (2 mols.) in glacial acetic acid solu-

tion, which is then boiled for a few minutes, ethylenediphthalimidine yields a *tribromide*, $C_{18}H_{16}O_2N_2Br_3$, unstable, yellowish-brown needles, decomp. 187° (rapidly heated), which is immediately decomposed by water with regeneration of the diphthalimidine. Chlorine does not attack ethylenediphthalimidine in glacial acetic acid or carbon tetrachloride, but in the former solvent together with ethyl ether iodine produces a *di-iodide*, $C_{18}H_{16}O_2N_2I_2$, dark brown prisms, m. p. 180—181°.

Ethylenediphthalimidine is converted into diphthalylethylenediimide by boiling with phosphorus pentachloride and phosphoryl chloride, and by heating with sulphur at 240—250° until hydrogen sulphide ceases to be evolved, yields 1:2:4:3-*dibenzoylene*-1:4:5:6-*tetrahydropyrazine* (annexed formula), brownish-orange needles, m. p. 202—203°. This substance, which is more easily obtained by heating a mixture of phthalide, ethylenediamine, and sulphur in a sealed tube at 250°, is oxidised to diphthalylethylenediimide by chromic and acetic acids.



Ethylenediamine (anhydrous or in 50% aqueous solution) reacts vigorously with the lactone of *o*-hydroxyphenylacetic acid (2 mols.), and it is preferable to add alcohol as a diluent; the product is NN'-*ethylenebis*-(o-*hydroxyphenylacetamide*),

$$C_2H_4(NH\cdot CO\cdot CH_2\cdot C_6H_4\cdot OH)_2,$$

colourless needles, m. p. 208°, which forms a *diphenylurethane*, $C_{32}H_{30}O_6N_4$, needles, m. p. 225°. Still more vigorously react 50% aqueous ethylenediamine and the lactone of *o*-hydroxydiphenylacetic acid, and alcohol must be added to keep the reaction under control; the product is N-o-*hydroxydiphenylacetylethylenediamine*, $OH\cdot C_6H_4\cdot CHPh\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2$, colourless needles, decomp. 197°, whether 1 or 2 mols. of the lactone is present. C. S.

Histidine and Carnosine. The Synthesis of Carnosine. LOUIS BAUMANN and THORSTEN INGVALDSEN (*J. Biol. Chem.*, 1918, **35**, 263—276).—The amino-radicle may be removed from carnosine by treatment in aqueous solution with barium nitrite and sulphuric acid. After hydrolysis, by boiling with sulphuric acid, 70% of the theoretical quantity of histidine can be isolated from the deaminised product. Carnosine must therefore be regarded as β-alanylhistidine,

$$\begin{matrix}NH\cdot CH\\ | \\ CH{=}N\end{matrix}\!\!>C\cdot CH_2\cdot CH(NH\cdot CO\cdot CH_2\cdot CH_2\cdot NH_2)\cdot CO_2H,$$

instead of the other possible isomeride, histidyl-β-alanine,

$$\begin{matrix}NH\cdot CH\\ | \\ CH{=}N\end{matrix}\!\!>C\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot CO_2H.$$

This conclusion has been confirmed by the synthesis of carnosine. A solution of β-iodopropionyl chloride in light petroleum is added

slowly to histidine dissolved in water, an alkaline reaction being maintained throughout by the addition of barium hydroxide. The reaction product is not isolated, but after the removal of the barium by means of carbon dioxide, the filtrate is saturated with ammonia, first in the cold and eventually in sealed tubes at 100°. By fractional precipitation with silver nitrate and barium hydroxide, about 3 grams of pure carnosine were obtained from 40 grams of histidine.

By a similar method, *β-iodopropionylalanine*,

$$CH_2I\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

is prepared by the interaction of α-alanine and β-iodopropionyl chloride. It melts at 153—155°.

Extracts of dog's liver and muscle, which readily hydrolyse certain dipeptides, do not hydrolyse carnosine.

Attempts to prepare histidyl-β-alanine, or derivatives of it, have not been successful. By the action of α-naphthalenesulphonyl chloride on histidine in alkaline solution, *α-naphthalenesulphonylhistidine naphthalenesulphonate*, $C_{26}H_{23}O_7N_3S_2,H_2O$, is obtained, which melts at 155°, and, on further heating, solidifies, and melts again at 220°. By heating at 150° over phosphoric oxide in a vacuum, the molecule of water is removed, and the anhydrous substance crystallises in long, prismatic rods from methyl alcohol containing a few drops of glacial acetic acid, and melts at 222°. By treatment of its alcoholic solution with sodium hydroxide, the compound yields *α-naphthalenesulphonylhistidine*,

$$C_{16}H_{15}O_4N_3S.H_2O,$$

m. p. 236°, $[\alpha]_D^{24}$ − 190·8°.

Hippuryl-β-alanine, $C_{12}H_{14}O_4N_2$, is readily prepared by the interaction of β-alanine and hippuryl chloride in alkaline solution. It crystallises in long needles, m. p. 183—185°. H. W. B.

Crystalline Form of 3 : 7-Dimethyl-1 : 9-diethyluric Acid and of its Glycol Dimethyl Ether. A Correction. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 255).—The description of the crystalline form of 3 : 7-dimethyl-1 : 9-diethyluric acid (A., 1917, i, 590) is really that of its glycol dimethyl ether. The former crystallises in small rhombohedra with blunted angles.

C. S.

Azo-dyes derived from *m*-Phenetidine. FRÉD. REVERDIN, AUG. RILLIET, and CAM. VERNET (*Arch. Sci. phys. nat.*, 1918, [iv], **46**, 74—80).—Benzenediazonium chloride combines with *m*-phenetidine to give *4-benzeneazo-m-phenetidine*

$$N_2Ph\cdot C_6H_3(OEt)\cdot NH_2,$$

m. p. 84—85°, yielding a *hydrochloride*, m. p. 152—153°, an *acetyl* derivative, m. p. 135°, and a *benzoyl* derivative, m. p. 146°. This base, when further diazotised and combined with β-naphthol, gives the *bisazo*-compound, $N_2Ph\cdot C_6H_3(OEt)\cdot N_2\cdot C_{10}H_6\cdot OH$, brown needles, m. p. 172°, with "R-salt," the *bisazo*-compound,

$$N_2Ph\cdot C_6H_3(OEt)\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH,$$

a reddish-violet powder, dyeing silk and wool reddish-violet, and with naphthionic acid the *bisazo*-compound,

$$N_2Ph\cdot C_6H_3(OEt)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2,$$

a blackish-brown powder, dyeing silk a reddish-brown, not fast to light. The base has also been diazotised and combined with 7-amino-1-naphthol-3-sulphonic acid, 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, 3-amino-2-naphthol-6-sulphonic acid, 2-naphthol-7-sulphonic acid, 1-naphthol-4-sulphonic acid, and 8-amino-1-naphthol-3 : 6-disulphonic acid.

Aniline-*m*-sulphonic acid similarly furnishes m-*sulphobenzene-azo*-m-*phenetidine*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_3(OEt)\cdot NH_2$, reddish-brown needles, m. p. 214—215°. This base, when further diazotised, combines with *p*-nitrobenzeneazo-8-amino-1-naphthol-3 : 6-disulphonic acid to give the *trisazo*-compound,

$$SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_3(OEt)\cdot N_2\cdot C_{10}H_2(OH)(NH_2)(SO_3H)_2\cdot N_2\cdot C_6H_4\cdot NO_2,$$

as a blackish-green powder.

In the same manner, *p*-nitroaniline yields p-*nitrobenzeneazo*-m-*phenetidine*, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OEt)\cdot NH_2$, which, when diazotised and combined with chromotropic acid, gives the *bisazo*-compound, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OEt)\cdot N_2\cdot C_{10}H_3(OH)_2(SO_3H)_2$, a blackish-brown powder, in which the nitro-group may be reduced by sodium sulphide, giving a brown powder, which dyes wool blue. *m*-Phenetidine does not apparently combine readily with diazonium salts of high molecular weight. W. G.

Influence of Substituents on Reactions. I. The Rate of Reduction of Substituted Phenylhydrazines. HARTWIG FRANZEN (*J. pr. Chem.*, 1918, [ii], **97**, 61—92).—It is already known that derivatives of the aminophenylhydrazines and the ethoxyphenylhydrazines readily undergo fission at the –N–N– linking, the effect being less marked when the substituent group is in the meta-position than when in the ortho- or para-position (Franzen, A., 1907, i, 321; Franzen and Fürst, 1914, i, 206; 1917, i, 58, 59; Franzen and Schmidt, this vol., i, 81). The reduction of substituted phenylhydrazines by stannous chloride and hydrochloric acid appears to be parallel to the above fission reaction in its susceptibility to influence by substituents, but, being more rapid, is more convenient for experimental investigation in the less reactive compounds. Examination of the rate of reduction of phenylhydrazine and its various methyl, chloro-, bromo-, iodo-, carboxylic, and sulpho-derivatives shows that the first four radicles which direct further substituents into the ortho- and para-positions, when in the 2- or 4-position to the hydrazine nucleus, increase the rate of reduction of phenylhydrazine, whereas the last two radicles, which direct further substituents into the meta-position, effect a diminution in the rate of reduction, whether they are in the 3- or 4-position. Radicles of the former class, with the exception of methyl, when in the 3-position likewise increase the velocity of reduction, but the effect is always less than that of the same radicle in the ortho- or para-position, thus corresponding with the observa-

tions already made on the ethoxy- and amino-phenylhydrazines. With the second group of substituents, the influence is always greater in the meta- than in the para-position; the ortho-compounds in these cases were not investigated, because their tendency to ring formation gives rise to complications. With methyl, chlorine, and bromine the influence is greater in the ortho- than in the para-position, but with iodine and ethoxyl the case is reversed. When placed in order of the magnitude of their influence, the relative position of the substituents is $NH_2 > OEt > Me, I > Br, Cl$, the substituents methyl and iodine, as also bromine and chlorine, possessing almost equal influence. A striking parallel exists *between the tendency of these substituents to facilitate further* substitution at the ortho- and para-positions, in which positions of the phenylhydrazine molecule they themselves increase the reactivity of the substance, whilst the class of substituents including the carboxylic and sulpho-groups reduces the tendency of a compound to further substitution, and directs the new group into the meta-position, in which position of the phenylhydrazine molecule they cause the least diminution in the reaction velocity. It is also of interest that the relative effect of the substituents amino, hydroxyl, methyl, chlorine, on the reduction of the aromatic halogen compounds by hydriodic acid falls into a similar order to that above (Klages and Liecke, A., 1900, i, 387). In view of the preceding results, Vorländer's conclusion (A., 1903, ii, 67), that the unsaturated groups in particular possess the power of increasing the reactivity of the substituted compound, is unjustified; this criticism is confirmed by the peculiarity that the nitro-group in 1-chloro-2:4-dinitrobenzene increases the reactivity of chlorobenzene towards ammonia, but not towards hydrogen, whereas the presence of the amino- or hydroxyl group barely affects the former reaction, but favours the latter. The author is of opinion that the increase in the reactivity of phenylhydrazine induced by any such radicle as the amino-group or hydroxyl group is due to the unsaturated nature of the main atom by which it is attached to the benzene ring, and further evidence in support of this view is adduced from the behaviour of 4-hydrazinostilbene, the investigation of which places the CHPh:CH-radicle between OEt and Me in the above order of influence: the phenyl radicle falls into the same position as the styryl radicle, as is indicated by an investigation of 4-hydrazinodiphenyl. The conclusion is therefore drawn that the series $NH_2 > OEt > Ph, CHPh\!:\!CH > Me, I > Br, Cl$ represents also the relative degree of unsaturation of the radicles concerned, and that the groups $\cdot SO_3H$ and $\cdot CO_2H$, which effect a reduction in the reactivity of phenylhydrazine, are in an especially saturated condition. On investigation of the reaction of benzyl chloride and its three methyl derivatives with sodium ethoxide, it is found that the case resembles that of phenylhydrazine and the tolylhydrazines, the ortho-derivative being more reactive than the para-compound, and both of these more reactive than the meta-derivative, which indeed is but little more reactive than the parent compound.

Evidence of a similar but less simple nature is supplied by the behaviour of phenyl acetate and the three tolyl acetates towards alcoholic sodium ethoxide, although on account of the presence of water in the commercial alcohol used, the change observed was one of hydrolysis; the relative reactivity of the parent phenyl compound and its three methyl derivatives is identical with that of benzyl chloride and its methyl derivatives.

4-*Hydrazinostilbene*, $CHPh:CH\cdot C_6H_4\cdot NH\cdot NH_2$, was obtained in the form of its *hydrochloride*, pearly leaflets, m. p. 254° (*decomp.*), from 4-aminostilbene by successive diazotisation and reduction; *benzylidene* derivative, $C_{21}H_{18}N_2$, yellow, crystalline powder, m. p. 208° (decomp.); *dibenzoyl* derivative, $C_{28}H_{22}O_2N_2$, colourless leaflets, m. p. 195°. When heated with dilute hydrochloric acid, the base yields 4-aminostilbene, stilbene, ammonia, and nitrogen. 4-Hydrazinodiphenyl under similar conditions yields only 4-aminodiphenyl and ammonia. D. F. T.

Aminohydrazines. V. *m*-Amino-*p*-tolyl-β-benzylhydrazine. HARTWIG FRANZEN and COELESTIN MONDLANGE (*Annalen*, 1917, **414**, 189—195. Compare A., 1917, i, 58, 59).—This aminohydrazine has been examined in order to ascertain whether the yellow colour and the capacity to form intensely coloured salts exhibited by *o*-aminophenyl-β-benzylhydrazine (*loc. cit.*) are general characteristics of such aminophenylbenzylhydrazines.

Benzaldehyde-*m*-nitro-*p*-tolylhydrazone in boiling ammoniacal alcoholic solution is treated with sodium hyposulphite, whereby *sodium* m-*amino*-p-*tolyl-β-benzylhydrazinesulphonate* and *benzaldehyde*-m-*amino*-p-*tolylhydrazone* are obtained, which are separated by boiling water, in which the former, pale yellow leaflets, m. p. 211°, is insoluble. It is decomposed by boiling *N*/2-sulphuric acid, yielding sulphur dioxide and benzaldehyde-*m*-amino-*p*-tolylhydrazone, which is then converted into phenylmethylbenziminazole and ammonia. *Benzaldehyde*-m-*amino*-p-*tolylhydrazone*, obtained from the hot aqueous filtrate (above), forms golden-yellow leaflets, m. p. 167°, is converted by cold 10% hydrochloric acid into phenylmethylbenziminazole and ammonia, and in boiling alcoholic solution is reduced by 3% sodium amalgam, yielding m-*amino*-p-*tolyl-β-benzylhydrazine*, $NH_2\cdot C_6H_3Me\cdot NH\cdot NH\cdot CH_2Ph$, intensely yellow needles, m. p. 87°, which forms yellow solutions in organic solvents and develops in alcoholic solution an intense magenta colour on the addition of a little dilute mineral acid. C. S.

Glacial Acetic Acid as a Solvent for Prussic Acid. Benzalhydrazinophenylacetonitrile and some Derivatives. J. R. BAILEY and R. H. PRITCHETT (*J. Amer. Chem. Soc.*, 1918, **40**, 1230—1235).—Benzylidenehydrazinophenylacetonitrile,

$$CHPh:N\cdot NH\cdot CHPh\cdot CN,$$

prepared by adding potassium cyanide to a solution of benzylideneazine in glacial acetic acid, forms colourless crystals, m. p. 114°

(Adamczewski, *Diss.*, Heidelberg, 1911, records yellow leaflets, m. p. 111—112°), and is converted by concentrated hydrochloric acid into the corresponding amide, m. p. 171° (to a yellow liquid) (Adamczewski, m. p. 165—167° with decomp.). The nitrile and the amide in glacial acetic acid solution are converted by potassium cyanate into *benzylidenecarbamylhydrazinophenylacetonitrile*, $CHPh:N\cdot N(CO\cdot NH_2)\cdot CHPh\cdot CN$, rectangular plates, m. p. 228° (decomp.), and the corresponding *amide*,

$$CHPh:N\cdot N(CO\cdot NH_2)\cdot CHPh\cdot CO\cdot NH_2,$$

prisms, m. p. 183° (decomp. at 193°), respectively. The latter is converted by boiling 10% potassium hydroxide and subsequent acidification with acetic acid into *1-benzylideneamino-5-phenylhydantoin*, $NH<\begin{matrix}CO\cdot N\cdot N:CHPh\\ CO\cdot CHPh\end{matrix}$, crystals, decomp. 245—250°, which loses benzaldehyde by heating with dilute sulphuric acid and yields *1-amino-5-phenylhydantoin*, decomp. 232°. C. S.

Pekelharing's Pepsin. IV. W. E. RINGER (*Arch. Néerland. Physiol.*, 1918, **2**, 571—593. Compare A., 1917, i, 233; 1916, i, 226).—In his previous experiments, the extent of proteolysis has been measured by the author by precipitating the proteins with tannic acid and estimating the nitrogen in the filtrate. It is now shown that these results are not quite accurate, because the amount of nitrogenous material precipitated by the tannic acid is found to vary considerably according to the concentration of the salts in the solution. The effect of the error is that the descent of the curve illustrating the course of the digestion is really less than has been represented. The former experiments have now been repeated, the concentration of salt being maintained constant. The optimum concentration of hydrogen ions for the digestion of the albumoses by pepsin varies from $p_H = 2.5$ in the case of protoalbumose to 4·1 for deuteroalbumose. These results are in harmony with the view that a combination occurs between enzyme and substrate, because the smaller the hydrolytic product, the larger will be the number of particles in solution, and the sooner the moment will arrive (that is, the lower the degree of acidity) at which all the particles of enzyme are combined with particles of substrate, which according to the author constitutes the maximum point in the curve representing the hydrolysis.

The importance of the electrical charge of the protein in determining the course of proteolysis is illustrated by experiments in which the effect is ascertained of the addition of various potassium salts on the digestion of protein by pepsin. The strongly negative ferrocyanide ion inhibits proteolysis to a much greater extent than either the chloride or the sulphate. H. W. B.

Action of Chymosin and Pepsin. IV. Action of the Enzymes on Sodium Caseinogenate. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 33—77. Compare A., 1915, i, 726, 911).—Two extracts of gastric mucous membrane may show

equal enzymic activity when tested by their power of coagulating milk, and yet show considerable differences in their digesting power on fibrin or white of egg. This want of parallelism is found also when the substrate chosen in each case is caseinogen, and the activity tested first in the presence of alkali and then in that of acid. In the former case, the solutions become opalescent and a precipitate forms, whilst albumoses are produced in considerable amount, and although there does not appear to be direct proportionality between the strength of the chymosin and the time in which the opalescence becomes of a definite degree or the precipitate is just perceptible, or between the quantity of chymosin present and the amount of albumose produced in a given time, yet the relative strengths of two chymosin solutions may be compared in either of these ways. The results can be interpreted most easily by regarding chymosin and pepsin as separate enzymes, and this view is confirmed by the fact that the differences observed between the coagulating and digesting powers of two extracts are exactly paralleled by the differences in their behaviour towards caseinogen in alkaline and acid solutions respectively. Thus, if one of two solutions of equal peptic power clots milk with greater rapidity than the other, then its action on caseinogen in alkaline solution is found to be much more marked and rapid than is the case with the other enzymic solution. H. W. B.

Digestibility of Heated and Unheated Caseinogen. OLOF HAMMARSTEN (*Arch. Néerland. Physiol.*, 1918, **2**, 658—663).—When caseinogen is dissolved in water with the addition of the minimum amount of alkali and the solution heated for an hour in an autoclave at about 116°, a small quantity of albumose is formed whilst the recovered caseinogen is found to be more readily digested than unheated caseinogen by pepsin in the absence of free hydrochloric acid (negative reaction with Congo-red). The inability of heated milk to maintain the growth of young rats (Funk and Macallum, A., 1916, i, 861) cannot therefore be ascribed to an altered structure in the constituent amino-acids of the caseinogen caused by the heating, and resulting in failure of digestion and utilisation in the body. These results indirectly confirm the hypothesis of the existence of thermolabile indispensable accessory substances in milk. H. W. B.

Influence of Neutral Salts on the Action of the Salivary Diastase. J. TEMMINCK GROLL (*Arch. Néerland. Physiol.*, 1918, **2**, 516—520).—Both the anion and the cation of a neutral salt exert an action on ptyalin, the former being the more potent. The order in which the cations may be arranged expressing their relative activating power corresponds with that in which they affect colloids generally. The order of the anions, however, differs from that which would be expected if the diastase was a simple colloid. Neutral salts affect, therefore, not only the degree of dispersion of the ptyalin, but have another action, depending probably on the colloidal state of the substratum. H. W. B.

Enzymes and Surface Action. W. M. BAYLISS (*Arch. Néerland. Physiol.*, 1918, **2**, 621—624).—The action of enzymes consists in the condensation on their surfaces by adsorption of the constituents of the reacting systems, including water. The effect of this concentration is to increase the rate at which the reactions take place and to diminish greatly the time taken for equilibrium to be attained. If the rate of action of an enzyme, such as urease, is a function of the amount adsorbed, the presence of an indifferent substance, which is adsorbed to a greater extent than carbamide, should delay the reaction. Saponin is adsorbed by charcoal to a greater extent than carbamide, and more carbamide is adsorbed by a given weight of charcoal from a pure carbamide solution than from one containing a mixture of carbamide and saponin. Applying these results to urease, it is found that the addition of saponin to a solution of carbamide containing urease delays the rate of action of the enzyme, although eventually the extent of hydrolysis of the carbamide is equal to that attained in the absence of the saponin. Bile salts and amyl alcohol produce similar effects. The inhibiting effect of saponin is greater at a low temperature than at a higher one, and the temperature coefficient of the reaction is increased, both phenomena being in harmony with the view that the saponin exerts its action by adsorption. The author's hypothesis does not seem to account for the specificity of enzymes, but without attempting to disregard this difficulty, he points out that the surface forces controlling adsorption are as yet too little known to warrant a dogmatic statement on this question.

H. W. B.

Some Naphthalene Derivatives. A. ARCHIBALD BOON and JAMES OGILVIE (*Pharm. J.*, 1918, **101**, 129—130).—When arsenic acid is heated with an arylamine, the latter may undergo oxidation, as in the preparation of magenta, or it may undergo conversion into an arylarsinic acid, $AsRO(OH)_2$, or even a diarylarsinic acid, AsR_2O_2H. When an intimate mixture of equal parts of α-naphthylamine and arsenic acid is crystallised from hot water, *α-naphthylamine hydrogen arsenate*, $C_{10}H_7{\cdot}NH_2,H_3AsO_4$, is obtained in long, colourless needles, m. p. 170°, which become purple on exposure to the atmosphere or when heated above 165°; the apparent molecular weight in alcohol is 156. If this arsenate is heated with four-ninths its weight of α-naphthylamine at 200° for a short time, 1-aminonaphthyl-4-arsinic acid is produced, together with an amorphous, purple *substance*, $C_{13}H_{11}ON$; this gives a violet solution in organic solvents, and is doubtless an oxidation product of the naphthylamine. The formation of the arsenate and its further conversion into an arsinic acid confirm the general view that the reaction yielding aminonaphthylarsinic acid occurs by the stages

$$C_{10}H_7{\cdot}NH_2 \longrightarrow C_{10}H_7{\cdot}NH_2,H_3AsO_4 \longrightarrow C_{10}H_7{\cdot}NH{\cdot}AsO(OH)_2 \longrightarrow NH_2{\cdot}C_{10}H_6{\cdot}AsO(OH)_2.$$

[See also *J. Soc. Chem. Ind.*, October.] D. F. T.

Physiological Chemistry.

Estimation of Buffer Effects in Measuring Respiration. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **35**, 237—240).—The indicator method of measuring respiration (Haas, A., 1917, i, 433) consists in placing organisms in a solution containing an indicator and observing changes in colour produced by the giving off of carbon dioxide. Since the acidity and colour are affected by substances having a buffer action, it is evident that when such substances are present the amount of buffer action must be measured. This can be done by the apparatus described by the author, which permits the addition of measured quantities of carbon dioxide to known volumes of liquid of which the p_H values are estimated before and after the addition of the carbon dioxide. H. W. B.

Estimations of the Tension of Carbon Dioxide in the Alveolar Air by the Henderson-Russel Modification of Haldane's Method, and their Application for Testing the Stimulability of the Breathing Centre. EUGEN JENNI (*Biochem. Zeitsch.*, 1918, **87**, 331—358).—By means of the modification by Henderson and Russel of Haldane's method, it was found that the carbon dioxide tension of alveolar air remained constant over prolonged periods. When the subject of experiment is used to the procedure, the variations amount to but 2—3 mm. of mercury; the method is not, however, well adapted to clinical purposes. In a case of emphysema investigated, the tension of carbon dioxide was high. The method can be employed for testing the irritability of the breathing centre. For inhibition, the drugs morphine and pantopone were employed; both cause marked increase in the tension of carbon dioxide in the alveolar air. The preparation of Pavon-Ciba, in corresponding therapeutic doses, causes little alteration in the tension, and its inhibitory action on the breathing centre is less than that of morphine or pantopone. Alcohol is an excitant of the inhibitory centre in the doses used by the author. S. B. S.

Narcosis and Oxygen Concentration. B. VON ISSEKUTZ (*Biochem. Zeitsch.*, 1918, **88**, 219—231).—The action of narcotics is independent of the oxygen concentration, and there is no marked difference in their action on tadpoles in water rich and poor in oxygen. During narcosis, the oxygen respiration of tadpoles diminishes from 18—40%. Ethylurethane and alcohol in narcotising doses cause the same amount of diminution. Potassium cyanide diminishes oxygen respiration to the extent of 30—40% without producing paralysis. Increased partial pressure of oxygen can increase the oxygen respiration of the tadpoles without inhibiting the action of narcotics; in fact, the oxygen consumption of the animals under deep narcosis in water rich in oxygen is greater

than that of non-narcotised animals in water with the normal amount of oxygen. S. B. S.

Estimation of the Methyl Groups attached to Nitrogen in the Blood. A. Kossel and S. Edlbacher (*Arch. Néerland. Physiol.*, 1918, **2**, 625—628).—The application of Pregl's micro-analytical method for the estimation of the methyl groups attached to nitrogen (see Edlbacher, this vol., ii, 336) to blood gives results which indicate that the ratio N/Me ranges in normal blood from about 17 to 20, which corresponds with about 5 methyl groups per 100 atoms of nitrogen present. In a few cases of pathological blood, the ratio is rather higher, reaching to 26 in pernicious anæmia. The coagulated protein of the blood does not contain any methyl attached to nitrogen, whilst the amount in caseinogen is about 0·4%. H. W. B.

Properties and Composition of Oöcytase. Guy W. Clark (*J. Biol. Chem.*, 1918, **35**, 253—262. Compare Robertson, A., 1912, ii, 573).—Preparations of oöcytase, the fertilising and cytolysing substance in mammalian blood sera, have been obtained containing protein as an impurity. On hydrolysis, oöcytase yields hypoxanthine and a pentose, but only a trace of phosphoric acid. The active constituent is destroyed by heat at a temperature between 73° and 80°, and by prolonged contact with alcohol. Oöcytase is neither hæmolytic, bactericidal, nor identical with alexin. The characteristic fertilising and cytolysing properties are probably to be associated with the nucleosidic structure of the oöcytase. H. W. B.

Existence in the Animal Body of Substances capable of Fixing Alkaloids. W. Storm van Leeuwen (*Arch. Néerland. Physiol.*, 1918, **2**, 650—657).—Pilocarpine dissolved in rabbit's serum does not excite a strip of intestinal muscle (cat) to the same extent as an aqueous solution of pilocarpine containing the same proportion of the drug. The neutralising effect of the serum only appears slowly, and reaches its maximum in about twenty-four hours. Sera from other animals are not so effective, that from the dog being quite inert. The neutralising action is due to fixation and not to destruction of the pilocarpine, because by suitable means all the alkaloid may be subsequently extracted from the serum and found to retain its original stimulating power in aqueous solution. The neutralising substances are present also in the liver and other organs of the body, and it is to their presence in differing amounts that the varying susceptibility of different animals to alkaloids is probably due. H. W. B.

Calcium and Magnesium Metabolism. V. Effect of Acid and other Dietary Factors. Maurice H. Givens (*J. Biol. Chem.*, 1918, **35**, 241—251. Compare this vol., i, 321).—Experiments on two dogs are described, the results of which indicate that the ingestion of either hydrochloric acid or sodium chloride pro-

duces a small increase in the elimination of calcium in the urine, although it does not appreciably affect the calcium balance. The excretion of magnesium is not affected in either case. H. W. B.

Autolysis of Animal Tissues. KARL GUSTAV DERNBY (*J. Biol. Chem.*, 1918, **35**, 179—219).—Yeast cells and various animal tissues (liver, spleen, pancreas, gastric mucous membrane, and leucocytes of dogs and pigs) all contain two kinds of proteolytic enzymes: (*a*) pepsin-like enzymes which hydrolyse proteins to peptones, but not further, and for the action of which the optimum hydrogen ion concentration is about $p_H = 3 \cdot 5$; (*b*) enzymes similar to trypsin or erepsin, which attack only peptones or peptides, and hydrolyse them to amino-acids. The optimum hydrogen-ion concentration for the latter enzymes is about $p_H = 7 \cdot 8$. In some tissues, one type of enzyme is present to a much greater extent than the other.

Autolysis in the case of the pancreas and the liver proceeds furthest when the p_H is maintained between 5 and 6, and appears to be due to the action of the above proteolytic enzymes, the maximum action being obtained when the degree of acidity is such that both types of enzymes are able to work simultaneously. Pieces of tissue which have been treated with weak acids and then transferred to an alkaline solution undergo autolysis much more readily than similar pieces placed straightway into the alkaline solution. This is due to the ability of the ereptic enzyme to break down the peptones formed by the peptic enzyme in the acid solution, although it is unable to hydrolyse the native protein. H. W. B.

Co-ferment of Fermentation in the Animal Body. II. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **102**, 1—32. Compare this vol., i, 242).—The co-enzyme of zymase appears to exist in almost all the tissues of the frog and rabbit. It is present in relatively the largest amount in frog's muscle; it is absent from blood-serum. It is most readily extracted by boiling water. Cold water extracts contain the co-enzyme, but an inhibitory substance is also present which is destroyed by boiling. The inhibitory substance exerts its action on zymase and not on the co-enzyme, and appears to be of a protein nature. The chemical properties of the co-enzyme in muscle resemble those associated with the co-enzyme in yeast. It is dialysable, not destroyed by boiling, precipitated by alcohol, adsorbed by charcoal, etc. The course of fermentation, using the muscle co-enzyme, is analogous to that observed when the co-enzyme from yeast is employed.

The respiratory substance (*loc. cit.*) which accelerates the oxidation process in muscle appears to be identical with the co-enzyme of yeast and muscle. A similar co-enzyme is also present in germinating peas. H. W. B.

The Constituents of Alcoholic Extracts of Organs which are Active in Wassermann's Reaction. FRITZ SILBERSTEIN (*Biochem. Zeitsch.*, 1918, **88**, 1—12).—Extracts of incompletely

autolysed organs are more active as "antigens" in the Wassermann reaction than are extracts of the fresh organ. If autolysis, however, proceeds too far, the extracts become inactive. Neither the fraction soluble in alcohol, but insoluble in ether (soaps), nor the fractions soluble in alcohol, ether, and acetone (fatty acids, fats, and cholesterol) of either fresh or autolysed livers give a reaction as marked as the whole extract. The fraction from fresh organs containing the lipoids gives as good results as the whole extract of the partly autolysed organ. The best reaction, however, is obtained by a mixture of the lipoid fraction with equivalent amounts of the fraction containing the soaps, fatty acids, and cholesterol. Treatment of the organ with trypsin or steapsin destroys its power of giving antigens; this function of the organs is not, however, altered by their treatment with pepsin-hydrochloric acid, ricin-lipase, or with dilute acid or alkali. S. B. S.

Biology of Silicic Acid and Aluminium Oxide in Birds' Feathers. MAX GONNERMANN (*Zeitsch. physiol. Chem.*, 1918, **102**, 78—84. Compare A., 1917, i, 494).—Feathers almost always contain silicic acid and aluminium oxide. The amounts vary considerably in different birds, and appear to depend largely on the content of these substances in the food. The largest quantity of silicic acid found was in the feathers of the dove, *Columba palumbus* (77% of the total ash), whilst the feathers of the jay, *Corvus glandarius*, contained the most alumina (2·46%). Apparently, the feathers constitute a storing place for both substances.

H. W. B.

Relation of the Quality of Proteins to Milk Production. IV. E. B. HART and G. C. HUMPHREY [with D. W. SMITH] (*J. Biol. Chem.*, 1918, **35**, 367—383. Compare A., 1917, i, 608).—Similar experiments to those already described have been carried out, the results of which indicate an approximate equality and efficiency of the proteins of gluten feed and oil meal as supplements to the proteins of corn meal and clover hay, an increased supplementing effect for distiller's grains, and an inferior efficiency for cottonseed meal, taken in relation to the quality and quantity of milk produced. H. W. B.

Effect of Heat on the Citric Acid Content of Milk. Isolation of Citric Acid from Milk. H. H. SOMMER and E. B. HART (*J. Biol. Chem.*, 1918, **35**, 313—318).—Citric acid can be obtained from cows' milk, after freeing the latter from fat and protein, in the form of calcium citrate; it is present to the extent of about 0·2% of the milk or 2% of the milk solids. Citric acid is not destroyed or transformed into an insoluble salt by heating the milk even in an autoclave at 15 lb. pressure for one hour. The loss in anti-scorbutic power observed on heating milk is therefore not due to the destruction of citric acid, but to the inactivation of the anti-scorbutic vitamine.

To estimate citric acid in milk, the caseinogen is precipitated by a dilute sulphuric acid solution of mercuric sulphate and the filtrate treated with dilute potassium permanganate solution. The citric acid is oxidised to acetonedicarboxylic acid, which is precipitated by the excess of mercury sulphate. The mercury in the precipitate is estimated by dissolving in hydrochloric acid and titrating with potassium cyanide and silver nitrate, using potassium iodide as indicator. H. W. B.

Attempt to Filter the Enzymes of Milk. JEAN PICCARD and MARY RISING (*J. Amer. Chem. Soc.*, 1918, **40**, 1275—1281).—Attempts have been made to sterilise milk by filtration so that it would be free from germs and suspended impurities, while the enzymes would be unchanged. Failure resulted because a filter could not be found with pores large enough to allow the passage through them of the colloidal enzyme without at the same time allowing the passage of bacteria.

In the course of the work it was found that the Schardinger enzyme remains in the liquid portion of the milk after the casein and the fat have been removed by a small amount of acid. If the casein is precipitated by stronger acids, the enzyme is precipitated with it, and by still more acid it is destroyed. C. S.

Action of Sugars on Bronchial Secretion. D. LO MONACO (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 103—109).—The fact that the subcutaneous injection of sugars in small doses largely increases, and in larger doses diminishes and may even entirely prevent, lactation in women, cows, goats, etc., and that similar modifications of other animal excretions are also produced in this way, has led the author to examine the effect of subcutaneous injection of sucrose on a patient exhibiting copious bronchial secretion. The injection was rapidly followed by a diminution in the amount of the bronchial secretion, which sometimes ceased completely, reappearing again when the injections were suspended. This effect of the injection of sugar may be of great importance in removing one of the principal causes of the spread of phthisis, namely, the ingestion and respiration of dried tubercular sputum. T. H. P.

Decomposition of Muconic and Adipic Acids in the Animal Body. YOSHITANE MORI (*J. Biol. Chem.*, 1918, **35**, 341—351).—Muconic and adipic acids injected subcutaneously into rabbits are excreted to a large extent unchanged in the urine.
H. W. B.

Formation of the Unsaturated Acids in the Animal Organism. I. Behaviour of *p*-Methoxyphenylpropionic Acid in the Organism of the Rabbit. IWAO MATSUO (*J. Biol. Chem.*, 1918, **35**, 291—296).—After the subcutaneous injection of *p*-methoxyphenylpropionic acid, anisic and glycylanisic acids were isolated from the urine, instead of the expected cinnamic acid derivatives (compare Dakin, A., 1909, ii, 684). H. W. B.

Formation of *p*-Hydroxyphenyllactic Acid in the Animal)rganism and its Relation to Tyrosine Catabolism. YASHIRO ⟨OTAKE [with ZENJI MATSUOKA] (*J. Biol. Chem.*, 1918, **35**, ;19—331).—When *l*-tyrosine or *p*-hydroxyphenylpyruvic acid is ,dministered to rabbits or men, *l*-hydroxyphenyllactic acid appears n the urine, accompanied occasionally by small amounts of the *l*-acid. The administration of *dl*-hydroxyphenyllactic acid is ollowed by the elimination of only the *d*-acid, the lævorotatory omponent being evidently destroyed to a certain extent in its assage through the body. H. W. B.

Relation between Nutrition and the Formation of Kynurenic Acid from Tryptophan. ZENJI MATSUOKA (*J. Biol. Chem.*, 1918, **35**, 333—339).—The rate of formation of kynurenic icid from tryptophan is almost constant in the rabbit, the injecion of 1 gram of tryptophan being followed by the elimination of etween 0·2 and 0·3 gram of kynurenic acid in the urine. Apparntly kynurenic acid is very stable in the animal body, and it annot take the place of tryptophan for the maintenance of utrition. The formation of kynurenic acid from tryptophan is ot therefore profitable from the point of view of nutrition.
H. W. B.

The Biological Action of Convolvulin and Jalapin. G. HEINRICH (*Biochem. Zeitsch.*, 1918, **88**, 13—34).—These substances re like the saponins and agaricin in that they exert a hæmolytic ction when they are in neutral solution. They are very sensitive o alkalis, however, and rapidly lose the hæmolytic action in the resence of a slight excess of alkali. The hæmolytic action could nly be demonstrated in vitro, but not in vivo, as no blood appeared n the urine after intravenous or subcutaneous injection; neither vas any purgative action observed. They are both specific poisons or fish. For purgative action, direct contact of the glucosides with he mucous membrane of the intestines is necessary. This action s also lost when the substances are treated with alkali, and the æmolytic action can therefore be used in testing the value of reparations as drugs. They are less sensitive to the action of nineral acids, as, in spite of the hydrolysis which ensues, the urgative action is not lost. In this respect, they are similar to he saponins. Like the saponins, too, they are only incompletely esorbed in the alimentary tract, and appear unchanged in the æces. S. B. S.

The Influence of Temperature on the Capillary Activity of Narcotics. B. VON ISSEKUTZ (*Biochem. Zeitsch.*, 1918, **88**, 213—218).—Temperature alters the narcotic activity of indifferent narcotics in the same direction as it alters their capillary activity. Increase and decrease of the narcotic activity of the six substances nvestigated by H. H. Meyer can be ascribed not only to the differnce produced in their distribution between water and organic

solvents on warming, but also to increase or decrease of their capillary activity. In the case of other poisons, increase of temperature can cause diminution of capillary activity, whilst their potency is enhanced. S. B. S.

Combined Action of Narcotics and Potassium Cyanide on Water-fleas. F. J. J. Buytendyk (*Arch. Néerland. Physiol.*, 1918, **2**, 521—529).—Warburg's theory of the action of narcotics on living cells is based on the assumption that the narcotic produces a modification in the degree of dispersion of the colloids in the cell. The combined action of two narcotics might be expected to be equal to the sum of the actions of each separately. This is found to be the case when narcotics such as alcohol and chloroform are employed, but not when one of the narcotics is potassium cyanide. Water-fleas live in 3% alcohol or 1·5% urethane for more than twenty-four hours; in a liquid containing 3% of alcohol and 1·5% of urethane, they do not live more than ten minutes. When alcohol and potassium cyanide are similarly tested, it is found that instead of alcohol increasing the toxicity of the cyanide, it actually diminishes it, and the smaller the percentage of alcohol in the mixture, between the limits 3% and ⅛%, the greater is the neutralising effect on the cyanide. It is conceivable that the narcotic might repel the hydrocyanic acid from the surface of the cell, but the author does not consider that an explanation on these lines is adequate to explain the observed facts. Moreover, the author has been unable to detect any similar neutralising action of narcotics on the inhibition by potassium cyanide of the phototropic phenomena observable with the *Daphniidæ*. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Anaerobic Culture Volumeter. Zae Northrup (*J. Ind. Eng. Chem.*, 1918, **10**, 624—625).—A glass bottle is closed by a cork through which passes a glass tube extending nearly to the bottom of the bottle and having a small Berkefeld filter fixed to its lower end. The tube has a tap just above the cork, and the upper end of the tube passes through a cork which fits into the neck of an inverted tapped separating funnel. The bottle is provided with a small exit tube plugged with cotton wool. The separating funnel is filled with liquid culture medium, and a quantity of the latter is introduced into the bottle so as to cover the filter. After the filled apparatus has been sterilised, the culture containing gas-forming organisms is pipetted into the stem of the funnel, admitted through the tap of the latter; this tap is then closed, the lower tap opened, and the stem of the funnel plugged with cotton wool.

The gas formed by the organisms collects under pressure in the funnel, and may be transferred to a gas burette for examination.

W. P. S.

The Influence of Dicyanodiamide on the Growth of various Micro-organisms. LUISE MOLLER (*Biochem. Zeitsch.*, 1918, **88**, 85—96).—Experiments were carried out with various wild yeasts, moulds, and bacteria, and these indicate that dicyanodiamide has no advantages as a sole source of nitrogen for organisms; on the contrary, it exerts a deleterious action on their growths.

S. B. S.

A Study of the Antiseptic Properties of certain Organic Compounds. I. J. KLIGLER (*J. Exp. Med.*, 1918, **27**, 463—478; from *Physiol. Abstr.*, 1918, **3**, 270—271).—An examination of the antiseptic properties of a number of organic compounds, including dyes of the triphenylmethane series. S. B. S.

The Formation of Ferments. VII. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **88**, 35—42. Compare this vol., i, 328). —The conditions for the formation of the catalase of *Proteus* were investigated. Whilst leucine is essential for the formation of urease by this species of bacteria, this is not the case for formation of the catalase. Other amino-acids, such as aspartic acid and alanine, can be employed, and a considerable development of this ferment takes place in a medium containing, besides the essential inorganic salts and one of these amino-acids, sodium lactate. The catalase acts after the bacteria have been killed (that is, in the presence of toluene). If inactivated by not too large quantities of mercuric chloride and too long a period of contact with this substance, its activity can be restored by treatment with potassium cyanide. S. B. S.

The General Relationship of Aldehydes to Alcoholic Fermentation. The Co-ferment of Yeast. CARL NEUBERG (*Biochem. Zeitsch.*, 1918, **88**, 145—204).—The author gives detailed experiments which confirm his previous statement that aldehydes generally accelerate the alcoholic fermentation by yeasts of dextrose and mannose. His experiments include a series of fatty aldehydes from formaldehyde up to decaldehyde, chloral hydrate, hydroxyaldehydes (aldol, acetopropionaldol), unsaturated aldehydes (citronellal and citral), aromatic aldehydes (benzaldehyde, *p-iso*propylbenzaldehyde, phenylacetaldehyde), aromatic hydroxy-aldehydes and their ethers (salicylaldehyde, *p*-hydroxybenz-aldehyde, anisaldehyde, piperonal, and vanillin, which is the only aldehyde which failed to give acceleration), the unsaturated aromatic aldehyde, cinnamaldehyde, cyclic aldehydes (furfur-aldehyde and *cyclo*citral), dialdehydes (glyoxal, *iso*phthalaldehyde, terephthalaldehyde), keto-aldehydes (methylglyoxal and phenyl-glyoxal), and aldehyde-acids. The author also confirms his former statement that a mixture of keto-acids with potassium phosphate acts as a co-ferment. He suggests that certain differences in results

on this point obtained by Harden (A., 1917, i, 501) may be due to the fact that the yeast preparations employed by the latter were not quite free from co-ferments. S. B. S.

Chromogenic Yeasts. New Biological Reaction for Iron. M. W. BEYERINCK (*Arch. Néerland. Physiol.*, 1918, **2**, 609—615).—Several yeasts containing lactase have the property of secreting under favourable conditions a colourless chromogen which, in the presence of a salt of iron and atmospheric oxygen, is converted into a red pigment. The "fat" yeast, *S. pulcherrimus*, which is characterised by its power of forming fat, does not contain lactase, but it nevertheless forms the above colourless chromogen and red pigment more readily and abundantly than any of the other yeasts. Since it occurs frequently on grapes and in heather honey, and can thus be easily obtained, it has been employed by the author for the preparation and examination of the chromogenic substance. If the yeast is grown on an iron-free medium, pigmentation does not occur. On adding a trace of an iron salt and exposing to air, the red coloration gradually appears. Inoculation of the yeast into a medium containing as little as 10 mg. of iron citrate in 100 c.c. is sufficient to cause the developing yeast cells to become surrounded with a pigmented halo, whilst with larger quantities of iron the cells themselves become red.

The pigment has acidic properties, forming colourless salts with strong bases, which when acidified again produce red solutions. It is a stable substance; its solution in dilute sulphuric acid may be boiled without the occurrence of any decomposition. It does not appear to belong to the anthocyanin or the carotinoid group of pigments. H. W. B.

Anæsthesia and Respiration. A. R. C. HAAS (*Science*, 1917, N.S., **46**, 462—464).—Using a method previously described (compare A., 1917, i, 433) for the estimation of small quantities of carbon dioxide in solution, the author finds that when *Laminaria* is exposed in sea-water to the action of anæsthetics, in sufficient concentration to produce a measurable effect, there is an increase in respiration. This may be followed by a decrease if the reagent is sufficiently toxic. No decrease is observed with low concentrations which are not toxic. W. G.

Photosynthesis. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1918, **5**, 105—111).—For the demonstration of photosynthesis, an apparatus is described which permits of the removal, at intervals, of satisfactory samples of the gases by which the leaf is surrounded, of the stirring and mixing of the gases when necessary, and of the analysis of the gases by a simple method which is sufficiently accurate for ordinary purposes. The apparatus is figured in the original. W. G.

A Simple Method of Measuring Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS (*Science*, 1918, *N.S.*, **47**, 420—422).—Minute amounts of photosynthesis can be accurately measured

by placing aquatic plants, such as *Ulva*, *Spirogyra*, *Hydrodictyon*, and *Potamogeton*, in solutions containing hydrogen carbonates with a little phenolphthalein, and observing the change in the colour of the indicator on exposure to sunlight. The method can be used for quantitative investigations or for demonstration purposes. W. G.

Methods of Studying Permeability of Protoplasm to Salts. S. C. BROOKS (*Bot. Gaz.*, 1917, **64**, 230—249).—A general discussion of the methods commonly used in the study of permeability, from which the steps most essential to further progress in the solution of the problem are considered to be: (1) an analysis of the various disturbing factors in the methods involving chemical estimations and the satisfactory interpretation of the results obtained by these methods; (2) a similar analysis of the methods depending on turgor, with special reference to the possible effect of exosmosis; (3) the establishment of methods determining progressive changes in permeability without the disadvantages attaching to the methods at present in use. The author considers that his diffusion method (compare following abstract) answers these requirements. W. G.

A New Method of Studying Permeability. S. C. BROOKS (*Bot. Gaz.*, 1917, **64**, 306—317).—The method described depends on the diffusion of salts or other substances through a diaphragm of living tissue. Two cells are prepared of glass tubing 18 mm. in diameter, one being 2·5 cm. and the other 4 cm. in length, the ends being ground flat. Between these two edges is placed the tissue, and the cells are rapidly filled with the necessary solutions in turn, and the apparatus set up vertically, the longer cell being at the bottom and closed by a rubber tube and clip, and the upper cell covered to prevent loss by evaporation. The permeability, as shown by the rate of passage of salts through the diaphragm, is measured by determining the changes in electrical conductivity of the two solutions. Where dead tissue is required for experiments on the permeability of the intercellular substance, living disks are exposed to an atmosphere saturated with chloroform vapour for sixteen to twenty-four hours. The results obtained with disks of *Laminaria Agardhii* indicate that the protoplasm of this kelp is normally permeable to the salts of sea-water. Sodium salts cause an increase of permeability, which culminates in death. Calcium and lanthanum salts cause a decrease in permeability, followed by an increase, which culminates in the death of the tissue. W. G.

Antagonism and Permeability. W. J. V. OSTERHOUT (*Science*, 1917, *N.S.*, **45**, 97—103).—Experiments show that all substances which affect permeability may be divided into two groups: (1) those which act like sodium chloride, (2) those which act like calcium chloride (compare Brooks, preceding abstracts). It was further found that substances which behave like sodium chloride

with respect to antagonism, in experiments on growth, behave like sodium chloride in their effect on permeability, and similarly for the second group. There is thus a striking parallel between effects on permeability and antagonistic effects in growth, and all solutions which permit normal growth also preserve normal permeability. The author discusses possible theoretical explanations of these facts and gives experimental data in support of his theory. W. G.

Does the Temperature-coefficient of Permeability indicate that it is Chemical in Nature? W. J. V. OSTERHOUT (*Bot. Gaz.*, 1917, **63**, 317—320).—The results of Stiles and Jörgensen (compare A., 1916, i, 108) indicate that permeability is chemical rather than physical in nature. From a brief, critical survey of their work, and taking into account his own work on the temperature-coefficient of permeability (compare *Biochem. Zeitsch.*, 1914, **67**, 272), the author does not accept the view that permeability is chemical in nature. W. G.

Similarity in the Effects of Potassium Cyanide and of Ether. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1917, **63**, 77—80).—When potassium cyanide is added to sea-water in which are tissues of *Laminaria Agardhii*, it first causes a temporary decrease in permeability, thus resembling, in this respect, anæsthetics such as ether, chloroform, and alcohol, but the concentrations of potassium cyanide necessary to produce a decrease of permeability are very much smaller than the corresponding concentrations of the latter substances. W. G.

The Antagonistic Action of Salts. L. W. H. VAN OYEN (*Biochem. Zeitsch.*, 1918, **87**, 418—424).—A preliminary account of attempts to correlate physical properties of salts in solution with their biological action. It is shown that chlorine is adsorbed less by various adsorbents from solutions containing sodium, potassium, and calcium chlorides than from a solution of sodium chloride alone. The proportions of the various cations in the experiments were those used by Osterhout in his biological experiments. Experiments are also described on diffusion of chlorine through a dialyser from solutions of sodium chloride alone or mixed with potassium and calcium chlorides. S. B. S.

The Reduction of Carbon Dioxide by Hydrogen Peroxide as the Basis of Assimilation by Plants. HANS WISLICENUS (*Ber.*, 1918, **51**, 942—965).—The reduction of carbon dioxide to formic acid, but not to formaldehyde, has been achieved by many chemists, among whom Bredig and Carter have been most successful from a practical point of view (A., 1914, i, 377). It is recognised, however, that there is no resemblance between the powerful agents employed in the laboratory and the forces at the disposal of the green plant. One agent which is always at hand in nature is hydrogen peroxide, and this is to be regarded as the substance which causes the transformation of carbonic acid into formic acid

(compare Kleinstück, this vol., ii, 107). With the exception of the per-acids, carbonic acid is the only carboxylic acid the anhydride and charged or uncharged anions of which have a peroxidic structure, and the mechanism of the formation of oxygen and formic acid is therefore a mutual deoxidation of two peroxides, a reaction which requires no expenditure of energy.

A series of experiments is described which shows that oxygen and formic acid are actually produced when carbonates are left with hydrogen peroxide, the best results being obtained with a saturated solution of potassium hydrogen carbonate and a 10% solution of hydrogen peroxide. The reaction in this case is represented thus:

$$H_2O_2 + {}^{H}_{K}\left[{}^{O}_{O}\!\!>\!CO\right] = H_2O + O_2 + H{\cdot}CO_2K.$$

According to the above view, the process is one which concerns anions, and therefore a formate should be produced around the anode during the electrolysis of a carbonate or hydrogen carbonate, for the peroxidic anion will be in contact with hydroxyl ions. This also has been proved experimentally, and it may be possible to find the most suitable conditions of voltage and amperage to study this anodic, peroxidic, "round-about reduction," as it is called, more thoroughly.

The second stage in the assimilation of carbon dioxide is the further reduction to formaldehyde. This requires energy (light), a special catalyst (chlorophyll), and other factors, and is altogether more difficult of achievement than the first step. J. C. W.

Influence of certain Organic Substances on the Development of Plants. II. G. Ciamician and C. Ravenna (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 38—42).—Further experiments (**A.**, 1917, i, 244, 681) have been made on the influence on beans, maize, beetroot, tobacco and lupin seeds, and plants of mandelonitrile, benzyl and salicyl alcohols (saligenin); potassium benzoate and salicylate; vanillin, eugenol, and tannin; alanine and asparagine; the potassium derivatives of uric acid and xanthine in comparison with caffeine; pyridine and piperidine in comparison with nicotine, and also quinine, strychnine, and morphine. In the germination experiments, use has been made also of cocaine, atropine, and oil of mustard; galvanised iron germinators were used, the seeds being placed on cotton, covered with filter paper, and moistened with 0·1% solutions of the substances mentioned.

The antithetic relations of mandelonitrile and strychnine are confirmed, and so also is the conclusion that the alkaloids in plants possess some unknown but very definite function, which may be that of vegetable hormones. Just as is the case in animals with which the adrenaline of the suprarenal glands is produced from tyrosine, so different species of plants would transform their original indifferent waste products so as to render them fitted for the specific functions they are to serve. T. H. P.

Nitrate and Nitrite Assimilation. XIII. Iron and Oxygen as necessary Agents for the Reduction of Alkali Nitrites by Auto-oxidisable Compounds. OSKAR BAUDISCH (*Ber.*, 1918, **51**, 793—805. Compare A., 1916, i, 699—702; 1917, i, 434).—In the last communication, the important discovery was recorded that when solutions of aldoses or ketoses are boiled with ferrous sulphate and *sodium carbonate*, *dark reddish-violet solutions* are obtained, containing iron in "internally-complex" union, which have specific reducing properties. For example, alkali nitrites may be reduced to nitric oxide and ammonia, which is again supposed to involve the hypothetical acid, NOH, as an intermediate stage. *It is now shown that the activity of the reducing solution is unaffected* by oxygen, which may be freely admitted while the nitrite is being boiled with the agent without preventing the reduction, and that, furthermore, if formaldehyde is added to the mixture, the distillate contains hydroxamic acid, produced according to the equation $CH_2O + NOH = OH\cdot CH\!:\!N\cdot OH$.

It is further demonstrated that pentoses, dihydroxyacetone, glycollaldehyde, lævulose, and maltose, in addition to the original dextrose and lactose, have the power of forming complex iron compounds which can reduce nitrites, but not nitrates, or nitrobenzene to *aniline*. *It is not necessary, however, to wait until the iron complex has been made from the carbohydrate; it may be applied* in the form of the deep violet-red solution obtained by adding ferric chloride to an alkaline solution of catechol-*o*-carboxylic acid. Using the iron in this form, it may be demonstrated that glycerol, glyceric acid, and mannitol cannot reduce nitrobenzene; in other words, only aldoses and ketoses (in this group of compounds) have the property. If the violet catecholcarboxylic acid complex is boiled with dextrose, the solution becomes more brownish-red, showing that the metal is transferred to the sugar molecule.

Developing the subject further, the author has found that not only aldoses and ketoses, but such compounds as catechol, quinol, pyrogallol, gallic acid, phloroglucinol, quercetin (representing yellow plant pigments), and chrysarobin (representing the anthranols) can reduce nitrites if internally complex iron is present. Now, all these compounds are known to be auto-oxidisable, that is, they take up oxygen and in the presence of water produce hydrogen peroxide (compare Bach, A., 1897, ii, 401; Engler. 1897—1901; Manchot, A., 1900, i, 300). This is an important consideration, for these compounds will only reduce nitrites in the presence of oxygen. For example, if a solution of 1 : 8-dihydroxyanthranol (used in cases of psoriasis under the name "cignolin") is boiled with sodium carbonate, a few drops of ferric chloride, and sodium nitrite, no ammonia or nitric oxide whatever passes over in the distillate if the apparatus is first filled with pure nitrogen, but reduction takes place as soon as oxygen is admitted, and ceases again if this gas is excluded once more. Only the sugars are capable of causing the reduction in the absence of oxygen, but

these can provide the necessary oxygen from their own molecules, as Wieland has indicated (A., 1913, i, 1304).

Special experiments emphasise the point again that traces of *iron* in the "complex" condition must be present. Manganese and copper are without influence. Some of the above polyhydroxyl compounds, like the sugars, can make complexes from iron hydroxides, but *not all of them*. *Phloroglucinol* is *unable so to* "mask" ferric hydroxide, but does make a complex if potassium ferricyanide is provided.

Some theoretical considerations as to these phenomena are offered, and the bearing of them on biochemical processes is mentioned. Particularly important is the power of these auto-oxidisable compounds to bring about oxidations on the one hand (for example, methyl alcohol to formaldehyde) and reductions of nitrites, in the presence of iron complexes, on the other. It is well known that such compounds are widely dispersed in nature—phloroglucinol in many green plants, catechol and quinol in leaf buds, gallic acid, tannin, chrysarobin, yellow pigments, and anthocyanins. It has been shown, furthermore, that the secretion of tanning substances increases when plants are cultivated under less favourable conditions, such as in the cold or dark. In the animal body, also, phenolic compounds with adjacent hydroxyl groups play an important part; for example, adrenaline, and the pigment-forming amino-acid, 3:4-dihydroxyphenylalanine (Bloch, A., 1917, i, 675). Likewise in therapeutics, especially in dermatology, such phenols exert effects that strong reducing or oxidising agents alone are incapable of.

J. C. W.

The Distribution of the Aluminium Ion in Plants. JULIUS STOKLASA [with J. ŠEBOR, W. ZDOBNICKÝ, F. TÝMICH, O. HORÁK, A. NĚMEC, and J. CWACH] (*Biochem. Zeitsch.*, 1918, **88**, 292—322).—Aluminium is widely distributed in plants. A large number of analyses are tabulated. The xerophytes contain only small amounts of aluminium, whereas the hydrophytes and hygrophilic plants contain relatively large quantities. The mesophytes when growing on dry soils are very poor in aluminium, but contain an appreciable quantity when growing on marshy ground.

S. B. S.

Direct Influence of the Sap elaborated by the Wild on the Cultivated [Plant], and the Action that Acid Solutions, Directly Absorbed, exert on the Plant. C. CAMPBELL (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 57—61).—According to Comes, the greater resistance normally shown by wild plants when compared with cultivated ones is due to the greater acidity of the juices of the former. In order to obtain information bearing on this hypothesis, the author has carried out preliminary experiments to ascertain: (1) the influence exerted on a cultivated stock by a wild

graft, and (2) the effect on plants of the direct absorption of acid solutions. T. H. P.

Occurrence of Carotin in Oil and Vegetables. Augustus H. Gill (*J. Ind. Eng. Chem.*, 1918, **10**, 612—614).—Carotin was found to be present in maize, squash, orange-peel, flax seed, mustard seed, black sesame seed, butter, tallow, palm oil, and grass, but not in rape seed, white sunflower seed, turnip, safflower, cotton seed, or turmeric. W. P. S.

Chemical Investigations on Elaphomyces hirtus. G. Issoglio (*Gazzetta*, 1917, **47**, ii, 31—48).—Analysis of *Elaphomyces hirtus* shows that it contains a *micosterol*, $C_{30}H_{54}O_3$, crystallising in silky, white needles, m. p. 265°; traces of unidentified alkaloids; mannitol; micoinulin, which gives no coloration with iodine and does not reduce Fehling's solution; para*iso*dextran, extractable by dilute alkali solution and coloured reddish-brown by iodine; fungin, containing 2·28% of nitrogen. The spores contain a brown pigment with 5% of nitrogen. T. H. P.

Carbohydrates in Mulberry Leaves. Sojirô Kawase (*Journ. Tokyo Chem. Soc.*, 1918, **39**, 245—294).—The carbohydrates in mulberry leaves are dextrose, lævulose, sucrose, starch, dextrin, araban, galactan, and cellulose. Of these, cellulose occurs in largest amount, next comes a viscous substance consisting of araban and galactan, whilst starch is present in relatively small amount. The nutriment for the silkworm is therefore not starch as is generally supposed. The viscous substance in the leaves does not contain albuminous matter. The changes in the amounts of carbohydrates in the leaves during the development of the plant, or according to the time of gathering the leaves, or during the drying after gathering were determined, and are discussed from the physiological point of view. S. H.

Biochemistry of Sea Weeds. Harald Kylin (*Zeitsch. physiol. Chem.*, 1918, **101**, 236—247. Compare A., 1915, i, 931).—Various kinds of algæ have been examined for the presence of soluble carbohydrates and laminarin. Of eight species of brown algæ, two, *Desmarestia aculeata* and *D. viridis*, contained laminarin, whilst in all the percentage of soluble carbohydrates was small. Four species of *Florideæ* were found to contain trehalose, but not mannitol. Of the *Chlorophyceæ* investigated, *Cladophora rupestris* contained 15% of soluble carbohydrates, including saccharose, and a lævorotatory polysaccharide resembling inulin. H. W. B.

Isolation and Identification of Stachydrin from Lucerne Hay. H. Steenbock (*J. Biol. Chem.*, 1918, **35**, 1—13. Compare A., 1917, i, 439).—A full account of work previously published. H. W. B.

Organic Chemistry.

Two New Trihydric Alcohols. Moritz Kohn and Viktor Neustädter (*Monatsh.*, 1918, **39**, 293—298).—It has already been found possible (Kohn, A., 1914, i, 74) by the action of magnesium methyl iodide on the lactone of $\alpha\gamma$-dihydroxy-$\alpha\gamma$-dimethyl-*n*-valeric acid to obtain $\beta\gamma\epsilon$-trihydroxy-$\beta\gamma\epsilon$-trimethyl-*n*-hexane. Form*iso*butyraldol, by successive treatment with sodium hydrogen sulphite and potassium cyanide (compare Glaser, A., 1904, i, 284), can be converted into the lactone of $\alpha\gamma$-dihydroxy-$\beta\beta$-dimethyl-*n*-butyric acid, b. p. 118—120°/12 mm., 237—241°/ord. pressure, which reacts with magnesium methyl iodide in a similar manner to the above compound, forming *$\alpha\gamma\delta$-trihydroxy-$\beta\beta\delta$-trimethyl*-n-*pentane*, $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CMe_2\cdot OH$, b. p. 152—155°/12 mm., 256—262°/ord. pressure, which slowly solidifies to a crystalline mass, m. p. 68—70°. When heated with 33% sulphuric acid, this compound yields a *substance*, $C_8H_{16}O_2$, b. p. 187—192°, of camphor-like odour, probably *4-hydroxy-3 : 3 : 5 : 5-tetramethyltetrahydrofuran*, $\begin{matrix} CH_2\cdot CMe_2 \\ | \\ O\text{——}CMe_2 \end{matrix}\!>\!CH\cdot OH$. The action of magnesium phenyl bromide on the lactone proceeds in an analogous manner, and yields *$\alpha\gamma\delta$-trihydroxy-$\delta\delta$-diphenyl-$\beta\beta$-dimethyl* - n - *butane*, microscopic needles, m. p. 130—133°. D. F. T.

Action of Phosphorus Trichloride on Aliphatic Alcohols. T. Milobendzki and A. Sachnowski (*Chemik Polski*, 1917, **15**, 34—37; from *Chem. Zentr.*, 1918, i, 911—912).—The action of phosphorus trichloride on any alcohol results in the immediate formation of the normal ester of phosphorous acid, which is decomposed by the liberated hydrogen chloride into acid ester and alkyl chloride, $PCl_3 + 3R\cdot OH = P(OR)_3 + 3HCl \longrightarrow OH\cdot P(OR)_2 + RCl \longrightarrow OR\cdot P(OH)_2 \longrightarrow P(OH)_3 + RCl$. The decomposition of alkyl phosphites into phosphorous acid and unsaturated hydrocarbons is a secondary reaction which occurs most readily with esters derived from tertiary alcohols (even at low temperature and under diminished pressure).

The authors have demonstrated that the reaction for the diagnosis of isomeric alcohols (action of dry hydrogen chloride on the alkyl phosphites) proceeds quantitatively and is not merely a qualitative test.

For the preparation of normal esters, the following method is recommended. The mixture of alcohol (3 mols.) and pyridine (3 mols.) is largely diluted with ether, and phosphorus trichloride (1 mol.) is added drop by drop to the ice-cold mixture. The precipitated pyridine hydrochloride is filtered. The following yields were obtained: trimethyl phosphite, b. p. 110—111·5°/745 mm.

(crude product, 70%; pure substance, 42·5%); triethyl phosphate, b. p. 155—156°/740 mm. (73%); tri-*n*-propyl phosphite, b. p. 82—84°/10 mm. (89%); *tri*-n-*butyl phosphite*, b. p. 122—123°/12 mm., D_0^{20} 0·92547, D_4^{20} 0·92530, D_{20}^{20} 0·92692 (96%).

Dialkyl phosphites are prepared by a similar method, except that only two molecules of pyridine are used for each molecule of phosphorus trichloride. The details are as follows: dimethyl hydrogen phosphite, b. p. 56—58°/10 mm. (ca. 35%); diethyl hydrogen phosphite, b. p. 72—73°/9 mm. (85%); di-*n*-propyl hydrogen phosphite, b. p. 91—92°/10 mm. (96%); *di*-n-*butyl hydrogen phosphite*, b. p. 124—125°/12 mm., D_4^{20} 0·99516, D_4^{20} 0·99503, D_{20}^{20} 0·99697 (97%).

Attempts have been made to prepare mono-alkyl phosphites by the action of phosphorus trichloride on the alcohols saturated with hydrogen chloride; a relationship between the product of the reaction and the degree of saturation of the alcohol has been traced, but this section of the work has not been completed.

The reaction between phosphorus trichloride and trimethylcarbinol has been similarly investigated. The formation of unsaturated hydrocarbons and of trimethylcarbinyl chloride is not observed during the action when three molecules of pyridine are used for each molecule of phosphorus chloride. The product, the composition of which corresponded fairly accurately with that required for $(C_4H_9O)_3P$, could not be distilled without decomposition, whereby di*iso*butylene, b. p. 102—103°/758 mm., tri*isobutylene*, b. p. 178—180°/752 mm., together with unchanged tributyl phosphite, were obtained. Di-*tert*.-butyl hydrogen phosphite is still more readily decomposed, yielding at 38° (30 mm.) di- and tri-*iso*butylene. H. W.

Action of Water on Dialkyl Phosphites. T. MILOBENDZKI and A. SACHNOWSKI (*Chemik Polski*, 1917, **15**, 48—55; from *Chem. Zentr.*, 1918, i, 912—913. Compare Milobendzki, A., 1912, i, 155).—The stability of dialkyl phosphites in aqueous solution and their electrical conductivity have been investigated. Hydrolysis of the esters, $OH·P(OR)_2$, with alkali or barium hydroxide in solutions which are not below 0·05*N* proceeds too rapidly for accurate measurement. The hydrolysis of the esters proceeds slowly in aqueous solution at 25°; measurements have been made for diethyl hydrogen phosphite and dipropyl hydrogen phosphite, for full details of which the original paper must be consulted. The velocity of hydrolysis is very high at first, then decreases, subsequently increases, and finally sinks.

The dialkyl hydrogen phosphites behave as neutral substances. They do not combine with ammonia even when nascent; their aqueous solutions are neutral to indicators. The conductivity of the aqueous solutions is small—about ten times that of the water. The electrical conductivity of an equimolecular mixture of dipropyl hydrogen phosphite and silver nitrate is less than the sum of their conductivities. In the first thirty to forty minutes, no reaction

appears to occur; subsequently, the silver salt, $OAg\cdot P(OPr)_2$, slowly commences to separate, but precipitation is not complete after forty hours. The silver salt is stable beneath the aqueous solution in the dark and does not begin to decompose for about forty hours. H. W.

Salts of Alkyl Hydrogen Phosphites. T. MILOBENDZKI and MARIE SZWEJKOWSKA (*Chemik Polski*, 1917, **15**, 56—65; from *Chem. Zentr.*, 1918, i, 913—914).—Barium monoalkylphosphites are prepared by the neutralisation of monoalkylphosphorous acids or the hydrolysis of dialkyl hydrogen phosphites. *Barium ethyl hydrogen phosphite*, $Ba[O\cdot P(OEt)\cdot OH]_2$, forms hygroscopic crystals; it is completely hydrolysed in warm aqueous solution. *Barium* iso*propyl hydrogen phosphite* is similar. *Ferric propyl hydrogen phosphite*, obtained by the action of ferric hydroxide on an excess of the ester in concentrated aqueous solution or by precipitation of the solution of the barium salt by ferric chloride, is very sparingly soluble in water. It is very slowly attacked by ammonia, rather more rapidly by dilute acids, but is only slowly soluble even in fuming hydrochloric acid. *Ferric* iso*propyl hydrogen phosphite* resembles the *n*-propyl salt. The ferric *iso*butyl and *iso*amyl hydrogen phosphites are similarly prepared. The monomethyl and monoethyl phosphites could not be obtained by precipitation. Cuprous dialkyl phosphites, $(OR)_2P\cdot OCu$, are obtained when cuprous oxide acts on an aqueous solution of excess of the ester in closed vessels. The reaction, $(OR)_2P\cdot OH + CuOH \longrightarrow (OR)_2P\cdot OCu + H_2O$, proceeds slowly and is complete in five days; simultaneously, the white cuprous salt is slowly oxidised to the blue cupric salt, copper being precipitated. Purification is effected by pouring the product into water, when the copper and copper oxide sink, the cupric salt passes into solution, and the cuprous salt collects on the sides of the vessel. The dry salts are stable. The *cuprous* salts of diethyl, dipropyl, and di*iso*propyl hydrogen phosphites are described. The silver salts of the dialkyl phosphites are obtained by the cautious addition of alkali or of a solution of a readily hydrolysed salt to an aqueous solution of equivalent quantities of silver nitrate and the requisite ester, or, preferably, by treatment of the solution of the dialkyl phosphite with ammoniacal silver nitrate and immediate neutralisation of the ammonia with nitric acid. The ester suffers a certain amount of hydrolysis, which is less marked when the second of the above methods is adopted. The silver salts are sparingly soluble in water, soluble in ammonia and alkalis. The diethyl and dipropyl salts have been particularly investigated. H. W.

Constitution of Dioxalomalonic Ester and other Acylated Esters. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1918, **51**, 1087—1106. Compare A., 1917, i, 627).—The discovery that the so-called "ethyl diacetylmalonate," $CAc_2(CO_2Et)_2$, is really to be regarded as ethyl β-acetoxyethylidenemalonate,

$OAc\cdot CMe\colon C(CO_2Et)_2$, raises the question whether genuine diacylmalonic esters can be obtained at all, and whether they may not perhaps be *present in small quantities in specimens of the isomeric* esters. In the case of the "dioxalomalonates," Scholl and Egerer (A., 1913, i, 588) have already considered the two alternatives, analogous with the above, and decided on a formula of the true diacylmalonate type, thus, $(CO_2R\cdot CO)_2C(CO_2R)_2$, and not

$$CO_2R\cdot CO_2\cdot C(CO_2R)\colon C(CO_2R)_2.$$

Their decision depended chiefly on the facts that the compounds in question did not immediately reduce alkaline permanganate and gave carbon monoxide on heating, but it is now shown that these arguments have no weight and that the optical properties of the esters agree with the alternative formula. The refractions and dispersions are abnormally high and agree with the enolic structure rather than with the methanetetracarboxylate type. Furthermore, "ethyl *oxalomalonate*" is *found by titration to exist to the* extent of 60% in the enolic form, $CO_2Et\cdot C(OH)\colon C(CO_2Et)_2$.

These results support the opinion, often expressed by Claisen, *that compounds of the type* $C(CO\cdot)_4$ *do not, generally speaking,* exist, but tend to undergo rearrangement into isomerides in which at least one carbonyl group is attached to oxygen. There are exceptions to this generalisation, however. Scholl and Egerer's methanetetracarboxylates and acetylmethanetricarboxylates have optical properties which agree with the type $C(CO\cdot)_4$. The latter esters are obtained by acetylating the sodiomethanetricarboxylates, and it appears that compounds of the above type can only be obtained from methanetricarboxylates, for if the alternative procedure is adopted, namely, acetylation of malonic esters, followed by treatment with chloroformic esters, the products are the enolic isomerides.

With the co-operation of Scholl and Egerer, the optical properties of pure specimens of their methanecarboxylates have been investigated. Ethyl methanetricarboxylate has b. p. 139°/14 mm., m. p. 27–29°, $D_4^{14\cdot2}$ 1·1091, n_α 1·42628, n_D 1·42828, n_β 1·43392, n_γ *1·43838, at 14·2°,* $E\Sigma_\alpha + 0\cdot24$, $E\Sigma_D + 0\cdot21$, $E\Sigma_\beta - \Sigma_\alpha + 2\%$, $E\Sigma_\gamma - \Sigma_\alpha + 1\%$. Ethyl methanetetracarboxylate has b. p. 185°/18 mm., D_D^{17} 1·1357, n_α 1·43300, n_D 1·43563, n_β 1·44085, n_γ 1·44561, at 17°, $E\Sigma_\alpha$ 0·36, $E\Sigma_D$ 0·36, $E\Sigma_\beta - \Sigma_\alpha$ 3%, $E\Sigma_\gamma - \Sigma_\alpha$ 4%. Dimethyl diethyl methanetetracarboxylate has $D_4^{17\cdot2}$ 1·1828, n_α 1·43098, n_D 1·43327, n_β 1·43891, n_γ 1·44350, at 17·2°, $E\Sigma_\alpha$ 0·39, $E\Sigma_D$ 0·40, $E\Sigma_\beta - \Sigma_\alpha$ 5%, $E\Sigma_\gamma - \Sigma_\alpha$ 2%. Ethyl acetylmethanetricarboxylate, $CAc(CO_2Et)_3$, has b. p. 263°/atm., 154°/11 mm., $D_4^{13\cdot1}$ 1·1277, n_α 1·43354, n_D 1·43562, n_β 1·44158, n_γ 1·44638, at 13·1, $E\Sigma_\alpha$ 0·37, $E\Sigma_D$ 0·35, $E\Sigma_\beta - \Sigma_\alpha$ 5%, $E\Sigma_\gamma - \Sigma_\alpha$ 4%, and is decomposed by phenylhydrazine and aniline in the cold, phenylacethydrazide and acetanilide being deposited.

These data show that the refraction and dispersion of the tetracarboxylates are somewhat abnormal, which might be expected of compounds with so many carbonyl groups in close proximity, but the abnormality is by no means of the same order as that revealed by enolic compounds. For example, *ethyl β-ethylcarbonatoethyl-*

idenemalonate, $CO_2Et\cdot O\cdot CMe{:}C(CO_2Et)_2$, the isomeride of ethyl acetylmethanetricarboxylate, which is prepared by the action of ethyl chloroformate on "ethyl acetylmalonate" in the presence of pyridine, or on the sodium compound of this ester, is a colourless oil with b. p. 166°/12 mm., $D_4^{13\cdot4}$ 1·1330, n_α 1·44821, n_D 1·45084, n_β 1·45835, n_γ 1·46441, at 13·4°, $E\Sigma_\alpha$ 0·50, $E\Sigma_D$ 0·51, $E\Sigma_\beta - \Sigma_\alpha$ 19%, $E\Sigma_\gamma - \Sigma_\alpha$ 19%. Scholl's ethyl oxalomethanetricarboxylate [ethyl β-ketoethane-ααβ-tetracarboxylate], $CO_2Et\cdot CO\cdot C(CO_2Et)_3$, is likewise not unduly abnormal; it has b. p. 201—202°/23 mm., $D_4^{15\cdot45}$ 1·1671, n_α 1·43820, n_D 1·44026, n_β 1·44627, at 15·45°, $E\Sigma_\alpha$ 0·48, $E\Sigma_D$ 0·46, $E\Sigma_\beta - \Sigma_\alpha$ 7%.

For the preparation of ethyl "oxalomalonate" and "dioxalomalonate," absolutely pure ethyl oxalyl chloride is essential, and the authors have found that the best method of preparation is that described by Diels and Nawiasky (A., 1904, i, 981). Ethyl "oxalomalonate" exists to the extent of about 61% as the enol,

$$CO_2Et\cdot CO\cdot CH(CO_2Et)_2 \rightleftharpoons CO_2Et\cdot C(OH){:}C(CO_2Et)_2,$$

and has $D_4^{15\cdot2}$ 1·1546, n_α 1·44514, n_D 1·44794, n_β 1·45562, n_γ 1·46229, at 15·2°, $E\Sigma_\alpha$ 0·47, $E\Sigma_D$ 0·48, $E\Sigma_\beta - \Sigma_\alpha$ 25%, $E\Sigma_\gamma - \Sigma_\alpha$ 27%, calculated for the enolic modification. Ethyl "dioxalomalonate" is in reality *ethyl β-ethyloxalatoethylene-ααβ-tricarboxylate*,

$$CO_2Et\cdot CO\cdot O\cdot C(CO_2Et){:}C(CO_2Et)_2,$$

and has $D_4^{14\cdot9}$ 1·1926, n_α 1·45378, n_D 1·45665, n_β 1·46452, n_γ 1·47138, at 14·9°, $E\Sigma_\alpha$ 0·83, $E\Sigma_D$ 0·84, $E\Sigma_\beta - \Sigma_\alpha$ 27%, $E\Sigma_\gamma - \Sigma_\alpha$ + 29%, and yields *carbon monoxide*, quantitatively, when heated. J. C. W.

Action of Hypochlorous Acid on Mesityl Oxide. K. SLAWIŃSKI (*Chemik Polski*, 1917, **15**, 106—110; from *Chem. Zentr.*, 1918, i, 915).—The *ketochlorohydrin*,

$$OH\cdot CMe_2\cdot CHCl\cdot COMe,$$

is obtained as a colourless oil which rapidly becomes red, violet, and finally brown with separation of water when a 1% solution of sodium hypochlorite is added to mesityl oxide dissolved in acetic acid; when 1 gram-mol. of hypochlorous acid is used, only 40% of the chlorohydrin is produced, but the yield may be increased to 60% by employing a 15—20% excess of hypochlorous acid. The chlorohydrin has b. p. 96—98°/32 mm., D_0^0 1·1452, D_0^{70} 1·1089. It is converted by acetic anhydride into the *chloroketone*,

$$CMe_2{:}CCl\cdot COMe,$$

b. p. 55—60°/20 mm. The ketochlorohydrin dissolves completely in 20% potassium carbonate solution in the course of a few days, and the product of the reaction consists almost entirely of the *keto-oxide*, $O<\begin{matrix}CMe_2\\ CH\cdot COMe\end{matrix}$, a pale yellow oil of unpleasant odour, b. p. 54—55°/15 mm., D_0^{15} 0·9749. When a 10% aqueous solution of the keto-oxide is treated with one drop of hydrochloric acid and then neutralised with potassium carbonate, the *compound*,

$$OH\cdot CMe_2\cdot CH(OH)\cdot COMe,$$

is formed as an oil, b. p. 99—100°/12 mm., which reduces Fehling's solution in the cold; it does not give crystalline derivatives with

phenylhydrazine or semicarbazide. The dibenzoyl *compound* has m. p. 112—113°. H. W.

Preparation of Alkylselenocarbamides. CHEMISCHE FABRIK VON HEYDEN (D.R.-P., 305262; from *Chem. Zentr.*, 1918, i, 976). —Alkylselenocarbamides are prepared by the action of hydrogen selenide on alkylcyanamides. The substances have a therapeutic value in the treatment of cancerous disease, and serve as intermediate products in the production of the more stable alkyl haloid additive compounds. *Allylselenocarbamide* forms almost colourless needles, m. p. 93°, which become superficially red owing to the separation of selenium; it unites with bromine and iodine and reduces alkaline permanganate. It is very sensitive to air and light. The *mercury* and *lead* salts eliminate selenium. *Ethylselenocarbamide* forms colourless needles, m. p. ca. 125°.
H. W.

Preparation of Derivatives of Alkylselenocarbamides. CHEMISCHE FABRIK VON HEYDEN (D.R.-P., 305263; from *Chem. Zentr.*, 1918, i, 976).—The alkylselenocarbamides combine readily with alkyl haloids to yield compounds in which the selenium is more firmly combined than in the parent selenocarbamides; they are more stable towards light and more soluble in water. Their composition is probably expressed by the formula

$$Alk\cdot NH\cdot C(NH_2)\colon SeI\cdot Alk.$$

The *compound* formed from allylselenocarbamide and ethyl iodide forms white leaflets, m. p. about 100°; the iodine is precipitated as silver iodide by silver nitrate. The selenium is not precipitated as lead or mercury selenide by lead or mercury salts, as in the case of allylselenocarbamide. The *compound* from ethylselenocarbamide and allyl bromide has m. p. 115°. H. W.

Acetyl Cyanide. ROLAND SCHOLL [with JOSEF ADLER] (*Monatsh.*, 1918, **39**, 240).—Acetyl cyanide is conveniently prepared by boiling a solution of oximinoacetone in carbon disulphide with a little more than the theoretical quantity of phosphorus pentoxide for three-quarters of an hour and then distilling; the yield is approximately 40%. D. F. T.

Organic Chemical Reagents. I. Dimethylglyoxime. ROGER ADAMS and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1918, **40**, 1281—1289).—Methods of manufacturing the less common organic chemicals are being thoroughly worked out at the University of Illinois, and full details of the processes will be published with the object of inducing manufacturers to take up the production of the more useful of such reagents.

The present communication deals with the manufacture of dimethylglyoxime. This substance can be made by several methods, but the only one that is easily and cheaply adapted for large scale production is that of Gandurin (A., 1908, i, 400). The paper describes (1) the preparation of hydroxylamine sulphate and

(2) of amyl nitrite, (3) methyl ethyl ketone, (4) the preparation of its oximino-derivative and (5) of dimethylglyoxime, (6) the purification of coloured dimethylglyoxime, and (7) the recrystallisation of dimethylglyoxime.

The removal of coloured impurities in dimethylglyoxime is effected by treating its saturated solution in 8% sodium hydroxide solution with an excess of concentrated ammonium chloride solution; the colourless precipitate of dimethylglyoxime is filtered immediately. The process is repeated if necessary. C. S.

Action of Magnesium and Zinc on Dichloromethylarsine. ENRIQUE V. ZAPPI (*Bull. Soc. chim.*, 1918, [iv], **23**, 322—324).—In the presence of anhydrous ether, magnesium does not act on dichloromethylarsine, but in the presence of water the two react violently, giving methylarsine, hydrogen, and methane, methylarsenide, $(CH_3As)_x$, being precipitated and magnesium chloride left in solution. Zinc produces a similar decomposition. W. G.

Hydrocarbo-bases and a Study of Organic Derivatives of Mercury and of Lead. LAUDER W. JONES and LOUIS WERNER (*J. Amer. Chem. Soc.*, 1918, **40**, 1257—1275).—Hydrides of metals and organo-metallic compounds react with acids and suppress hydrogen ions; for example, (1) $NaH + HX = NaX + H_2$, (2) $Zn(CH_3)_2 + 2HX = ZnX_2 + 2CH_4$. If this property is sufficient reason for classifying these substances as bases, the former may be termed hydrogen bases and the latter hydrocarbo-bases. When compared with aquo-bases (KOH) and ammono-bases (KNH_2), the striking resemblance in chemical behaviour of these substances towards hydrogen ions seems to demand some factor common to all as the cause of the analogy, and the authors endeavour to find this factor in the theory of the electron conception of valency and Fry's theory of electromers (A., 1911, i, 431). The most obvious explanation of the similar reactivity of these various classes of bases would be to consider all groups combined with the metallic atoms in these compounds negative in the electronic sense. Whilst the organo-metallic compounds resemble aquo-bases and ammono-bases in certain other respects, as, for example, in forming basic salts and in undergoing double decomposition in reactions, they and the hydrogen bases differ from these in one important respect—they are powerful reducing agents. This property is explained by the powerful tendency of negative hydrogen to become positively charged and of negative alkyl groups (or of a carbon atom in them) to lose negative electrons and to assume positive charges.

Mercury diethyl is known to dissociate at about 200° to give mercury and butane. The dissociation, considered electronically, implies that one of the alkyl groups functions negatively and the other positively. $Hg^{-}_{+}{}^{+Et}_{-Et} \longrightarrow Hg + Et^{-} . {}^{+}Et$. Such groups should therefore exhibit differences in chemical reactivity, and this is

shown to be the case. Oxidation with permanganate removes only *one group*, *R·Hg·OH being formed*, and mercury dibenzyl, heated with glacial acetic acid at 160—170°, yields mercury, toluene, and benzyl acetate, together with some dibenzyl. Benzyl mercuriacetate under the same conditions gives only mercury and benzyl acetate, toluene and dibenzyl not being formed. Similar results are obtained with mercury diethyl and mercury di*iso*amyl, mercury, ethane or pentane, and ethyl or *iso*amyl acetate being obtained. Mercury diphenyl and mercury dimethyl give mercury and hydrocarbons, the acetate of the phenol or alcohol not being formed.

Similarly, tetra-alkyl lead compounds react as though three of the alkyl gronps were negative and the fourth positive. Thus, lead tetraethyl heated with glacial acetic acid at 250—260° gave lead acetate, ethane (in amount corresponding with three ethyl groups), and ethyl acetate. Results of the same kind were obtained with lead tetramethyl. C. S.

Dibromopyranthrone and Attempts to Prepare Benzanthrones. ROLAND SCHOLL (*Monatsh.*, 1918, **39**, 231—236).—[With W. NEUBERGER.]—The *substance obtained from* pyranthrone by the action of bromine at 100° is a *dibromo*-compound, $C_{30}H_{12}O_2Br_2$.

[With W. TRITSCH.]—2-*Iodo*-1-*methylnaphthalene*, $C_{11}H_9I$, pearly leaflets, m. p. 51·5°, prepared from 1-methyl-2-naphthylamine by the diazo-reaction, when heated with finely divided copper at 220—260° undergoes conversion into 1:1′-*dimethyl*-2:2′-*dinaphthyl*, $C_{22}H_{18}$, colourless needles, m. p. 230°. The corresponding *dibenzyl*-2:2′-*dinaphthyl*, $C_{34}H_{26}$, and *di*-p-*chlorobenzyl*-2:2′-*dinaphthyl*, $C_{34}H_{24}Cl_2$, obtained by heating benzyl chloride and *p*-chlorobenzyl chloride, respectively, with 2:2′-dinaphthyl in the presence of zinc chloride, were not pure snbstances. D. F. T.

2-Methylanthracene. ROLAND SCHOLL [with JOS. LENKO] (*Monatsh.*, 1918, **39**, 237—238).—2-*Methylanthracene*, $C_{15}H_{12}$, m. p. 206—207°, can be obtained by the action of hydriodic acid and phosphorus on 2-methylanthraquinone. D. F. T.

Derivatives of Fulvene. V. Condensation of Indene with Ketones. JOHANNES THIELE and KARL MERCK (*Annalen*, 1918, **415**, 257—273. Compare A., 1906, i, 569, 571, 586, 639). —The reactivity of the methylene group in *cyclo*pentadiene, indene, and fluorene decreases as the ethylenic linkings of the 5-ring become double linkings in a benzene nucleus. It has already been shown (*loc. cit.*) that *cyclo*pentadiene condenses extraordinarily easily with ketones, whilst fluorene does not condense at all under the influence of alkaline condensing agents. The behaviour of indene has now been examined. It condenses easily with acetone in the presence of methyl-alcoholic potassium hydroxide, yielding, after boiling for two hours, dimethylbenzfulvene (*picrate*, yellow needles, m. p. 115—116°, sintering at 102°), but at the ordinary temperature, after a week, a mixture of this and *ωω-dimethyl-3-a-*

hydroxyisopropylbenzfulvene, $C_6H_4<\begin{matrix}C(:CMe_2)\\C(CMe_2\cdot OH)\end{matrix}>CH$, m. p. 97—98°. Dimethylbenzfulvene is not reduced by aluminium amalgam and moist ether, but is smoothly converted into 3-*isopropylindene*, $C_6H_4<\begin{matrix}CPr^{\beta}\\CH_2\end{matrix}>CH$, faintly yellow oil, b. p. about 230° (decomp.) or 113°/15 mm., by sodium and boiling absolute alcohol.

Indene condenses less readily with aromatic ketones than with acetone. By prolonged boiling with acetophenone and alcoholic sodium ethoxide, it yields ω-phenyl-ω-methylbenzfulvene, yellow crystals, m. p. 68—69°, b. p. 178—179°/5 mm., and by similar treatment it condenses with benzophenone to give ωω-diphenylbenzfulvene (Grignard, A., 1911, i, 193). These two substances are reduced by aluminium amalgam and moist ether to 3-*α-phenylethylindene*, $C_6H_4<\begin{matrix}C(CHMePh)\\CH_2\end{matrix}>CH$, b. p. 161°/5 mm. and 196°/15 mm., and 3-*benzhydrylindene*, colourless crystals, m. p. 113—114°, respectively. The colours of the three preceding benzfulvenes conform to expectation; they are less intensely coloured than the corresponding fulvenes, and are more intensely coloured than the corresponding dibenzfulvenes (fluorene derivatives).

3-*iso*Propylindene condenses smoothly with benzaldehyde and with anisaldehyde in the presence of 27% methyl-alcoholic potassium hydroxide to form, after about twenty-four hours at the ordinary temperature, 1-*benzylidene*-3-*isopropylindene*,

$$C_6H_4<\begin{matrix}CPr^{\beta}\\C(:CHPh)\end{matrix}>CH,$$

yellow needles, m. p. 105·5°, and the corresponding *methoxybenzylidene* compound, yellow crystals, m. p. 81°, respectively. According to Thiele and Bühner's theory of the oscillating linking (A., 1906, i, 571), the latter of these two compounds ought also to be formed by the condensation of 3-*p*-methoxybenzylindene and acetone, but the product proves to be 3-p-*methoxybenzyl-ωω-dimethylbenzfulvene*, $C_6H_4<\begin{matrix}C(:CMe_2)\\C(CH_2\cdot C_6H_4\cdot OMe)\end{matrix}>CH$, faintly coloured, felted needles, m. p. 83°. This, like other aliphatic fulvenes, is not reduced by aluminium amalgam and moist ether, but is converted by sodium and boiling absolute alcohol into p-*methoxybenzylisopropylindene*, pale yellow oil, b. p. 200°/6 mm., which is also obtained by reducing 1-methoxybenzylidene-3-*iso*propylindene with aluminium amalgam and moist ether. The condensation of benzaldehyde with 3-*p*-methoxybenzylindene and of anisaldehyde with 3-benzylindene (Thiele and Bühner, *loc. cit.*) has therefore been re-examined, and it is now found that the two reactions do not give rise to the same substance under suitable conditions. When the condensations are effected by the prolonged action of methyl-alcoholic potassium hydroxide at the ordinary temperature, the same product, 3-benzyl-1-*p*-methoxybenzylidene-

indene, is obtained in both cases, but when the first pair of substances is boiled with methyl-alcoholic potassium hydroxide for only two to three minutes, 3-p-*methoxybenzyl*-1-*benzylideneindene*, $C_6H_4<\begin{matrix}C(:CHPh)\\C(CH_2\cdot C_6H_4\cdot OMe)\end{matrix}>CH$, yellow crystals, m. p. 89—90°, is obtained, which is readily changed to 3-beuzyl-1-*p*-methoxybenzylideneindene by the further action of boiling methyl-alcoholic potassium hydroxide. 3-Benzyl-1-*p*-methoxybenzylideneindene is not changed by prolonged boiling with methyl-alcoholic potassium hydroxide, and the same is the case with 3-*p*-methoxybenzyl-ωω-dimethylbenzfulvene and with 1-*p*-methoxybenzylidene-3-*iso*propylindene.

3-α-Phenylethylindene (indenylmethylphenylmethane) condenses with anisaldehyde in the presence of methyl-alcoholic potassium hydroxide at the ordinary temperature to form a *benzfulvene*, yellow needles, m. p. 121°, but whether this is ω-phenyl-3-*p*-methoxybenzyl-ω-methylbenzfulvene or 3-α-phenylethyl-1-*p*-methoxybenzylideneindene cannot be stated, because the condensation of 3-*p*-methoxybenzylindene and acetophenone to produce the other isomeride could not be effected. 3-Benzhydrylindene and anisaldehyde similarly condense to form a *benzfulvene*, yellow needles, m. p. 147°, which may be ωω-diphenyl-3-*p*-methoxybenzylbenzfulvene or 3-benzhydryl-1-*p*-methoxybenzylideneindene. C. S.

Condensation of Arylated Indenes with Aldehydes. WALTHER BERNTHSEN (*Annalen*, 1918, **415**, 274—290. Compare Thiele and Merck, preceding abstract).—Since Thiele and Bühner's theory of the oscillating linking has been disproved in the case of the two pairs of isomeric benzfulvenes (*loc. cit.*), it becomes of interest to introduce other aromatic groups in place of phenyl and anisyl, and to ascertain the effects of these on the position of the double linking, that is, the stability of the isomerides. The isomeric pairs are obtained quite simply: (1) indene is condensed with aldehyde *A*, the product is reduced by aluminium amalgam, and the reduction product condensed with aldehyde *B*; (2) indene is condensed with aldehyde *B*, the product reduced, and then condensed with aldehyde *A*. The condensations in all cases are effected by boiling methyl-alcoholic potassium hydroxide. The aldehydes used are benzaldehyde, *p*-tolualdehyde, *p*-*iso*propylbenzaldehyde, *p*-chlorobenzaldehyde, and 2:4-dichlorobenzaldehyde. Anisaldehyde was not employed, because 3-*p*-methoxybenzylindene isomerises during the condensation to anisylidenehydrindene for the most part.

Indene and *p*-chlorobenzaldehyde yield 1-p-*chlorobenzylideneindene*, $C_6H_4<\begin{matrix}C(:CH\cdot C_6H_4Cl)\\CH\end{matrix}>CH$, yellow needles, m. p. 116—117°, which is reduced by moist ether and aluminium amalgam to 3-p-*chlorobenzylindene*, colourless crystals, m. p. 71—73°. Indene and 2:4-dichlorobenzaldehyde yield a mixture of 1-op-*dichlorobenzylideneindene*, yellow crystals, m. p.

98·5—99·5°, and 3-op-*dichloro-α-hydroxybenzyl*-1-op-*dichlorobenzylideneindene*, $C_6H_4<\begin{matrix}C(:CH\cdot C_6H_3Cl_2)\\C(CH[OH]\cdot C_6H_3Cl_2)\end{matrix}>CH$, yellow crystals, m. p. 204—205°; the former of these, which is the more soluble in methyl alcohol, yields 3-op-*dichlorobenzylindene*, colourless crystals, m. p. 99—101°, by reduction. 3-*op*-Dichlorobenzylindene and *p*-chlorobenzaldehyde yield 3-op-*dichlorobenzyl*-1-p-*chlorobenzylideneindene*, $C_6H_4<\begin{matrix}C(:CH\cdot C_6H_4Cl)\\C(CH_2\cdot C_6H_3Cl_2)\end{matrix}>CH$, yellow crystals, m. p. 114—115° (in this and in other condensations in which a mono-substituted indene reacts with the second aldehyde, the boiling with the methyl-alcoholic potassium hydroxide is not prolonged beyond a few minutes), which is converted by the further action of boiling methyl-alcoholic potassium hydroxide into 3-p-*chlorobenzyl*-1-op-*dichlorobenzylideneindene*,

$$C_6H_4<\begin{matrix}C(CH_2\cdot C_6H_4Cl)\\C(:CH\cdot C_6H_3Cl_2)\end{matrix}>CH,$$

yellow crystals, m. p. 175—177°; the last substance is obtained directly from 3-*p*-chlorobenzylindene and *op*-dichlorobenzaldehyde, and is unaffected by boiling methyl-alcoholic potassium hydroxide.

3-*op*-Dichlorobenzylindene and benzaldehyde yield 3-op-*dichlorobenzyl*-1-*benzylideneindene*, yellow crystals, m. p. 73—74°. 3-Benzylindene and *op*-dichlorobenzaldehyde yield 3-*benzyl*-1-op-*dichlorobenzylideneindene*, yellow crystals, m. p. 117—118°. Each of this pair of isomeric benzfulvenes is quite unaffected by boiling methyl-alcoholic potassium hydroxide, 5% sodium methoxide solution, or concentrated ammonia solution.

Indene and *p*-tolualdehyde yield 1-p-*tolylideneindene*, yellow crystals, m. p. 91—92°, which is reduced to 3-p-*methylbenzylindene*, almost colourless crystals, m. p. 27—29°, b. p. 218—222°/12 mm., by aluminium amalgam. 3-*p*-Methylbenzylindene and benzaldehyde yield 3-p-*methylbenzyl*-1-*benzylideneindene*, yellow crystals, m. p. 106—107°. 3-Benzylindene and *p*-tolualdehyde yield 3-*benzyl*-1-p-*tolylideneindene*, yellow crystals, m. p. 98—100°. Each of this pair of isomerides gave by boiling with methyl-alcoholic potassium hydroxide a substance, m. p. about 70°, which is doubtless a mixture of the two isomerides.

Indene and *p*-*iso*propylbenzaldehyde gave 1-p-iso*propylbenzylideneindene*, orange-yellow crystals, m. p. 60—61°, which yields 3-p-iso*propylbenzylindene*, almost colourless crystals, m. p. 32°. 3-*p*-*iso*Propylbenzylindene and benzaldehyde yield 3-p-iso*propylbenzyl*-1-*benzylideneindene*, yellow needles, m. p. 105—107°. 3-Benzylindene and *p*-*iso*propylbenzaldehyde yield 3-*benzyl*-1-p-iso*propylbenzylideneindene*, yellow needles, m. p. 93—94°, which is converted into a mixture, m. p. 71—73°, of the two isomerides by prolonged boiling (ten hours) with methyl-alcoholic potassium hydroxide.

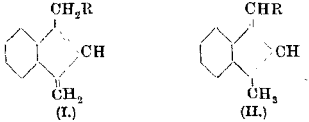
3-*p*-Chlorobenzylindene and benzaldehyde yield 3-p-*chlorobenzyl*-1-*benzylideneindene*, yellow needles, m. p. 98—99°, and 3-benzyl-

indene and *p*-chlorobenzaldehyde yield *3-benzyl-*1-p-*chlorobenzylideneindene,* yellow needles, m. p. 88—89°. The last compound is converted by boiling for eight hours with methyl-alcoholic potassium hydroxide partly into a mixture, m. p. 79—81°, of the two isomerides and partly into *3-benzyl-*1-p-*chlorobenzylindene,* colourless needles, m. p. 183—184°, which is also produced by reducing the benzfulvene with aluminium amalgam and moist ether.

3-*p*-Methylbenzylindene and *p*-chlorobenzaldehyde yield 3-p-*methylbenzyl-*1-p-*chlorobenzylideneindene,* large yellow crystals, m. p. 95—96°, together with a small quantity of a *substance,* colourless needles, m. p. 181—183°, which is probably 1-p-*chlorobenzyl-3-p-methylbenzylindene.* 3-*p*-Chlorobenzylindene and *p*-tolualdehyde yield a mixture of a colourless substance, m. p. 182—184° (which is shown to be 1-*p*-chlorobenzyl-3-*p*-methylbenzylindene), and a small quantity of a yellow substance, m. p. 91—92°, which appears to be 3-*p*-methylbenzyl-1-*p*-chlorobenzylideneindene in a not quite pure state. C. S.

Isomerism of Benzfulvenes and Indenes. H.-M. Wüest (*Annalen,* 1918, **415**, 291—337. Compare two preceding abstracts).—With regard to the eight pairs of isomerides described by Thiele and Merck and by Bernthsen (*loc. cit.*), no generalisation in respect of the stability of one of the two isomerides can be drawn, partly because no conclusions can be made from the nature of the groups introduced and partly because the transformation from the one isomeride into the other indubitably occurs only in two cases and fails entirely only in two other cases. A new series of benzfulvenes has therefore been examined.

The simplest case of isomerism is represented by a 3-substituted benzfulvene (formula I) and the isomeric ω-substituted 3-methylbenzfulvene (formula II).



3-*Methylbenzfulvene,* $C_6H_4<{CMe \atop C(:CH_2)}>CH$, an unstable, faintly yellow, intensely odorous oil, b. p. 102—104°/11 mm. (*picrate,* yellow needles, m. p. 125·5—126·5°), is readily obtained by boiling a mixture of 3-methylindene, paraformaldehyde, absolute alcohol, and 28% methyl-alcoholic potassium hydroxide for twelve minutes, but in no other case could a 3-substituted benzfulvene, of type I be obtained, the product being always the ω-substituted 3-methylbenzfulvene of type II, owing to the isomerising action of the alkali used as condensing agent.

Thus 3-benzylindene and paraformaldehyde yield 1-benzylidene-3-methylindene (*picrate*, pale red needles, m. p. 90—91°), 3-*p*-methoxybenzylindene and formaldehyde yield a mixture of 1-*p*-anisylidene-3-methylindene and 1-*p*-*anisylidene-3-ethylindene*, $C_{19}H_{18}O$, yellow needles, m. p. 100·5—101·5° (neither of these is changed by boiling for eight hours with methyl-alcoholic potassium hydroxide), 3-methylindene and furfuraldehyde yield, after condensation with methyl-alcoholic potassium hydroxide for forty-two hours at the ordinary temperature, 1-*furfurylidene-3-methylindene*, deep yellow needles, m. p. 77—77·5° (this compound, which forms a *picrate*, dark red needles, m. p. 97—98°, is also obtained by boiling 3-furylmethylindene, paraformaldehyde, absolute alcohol, and methyl-alcoholic potassium hydroxide for a few seconds and cooling rapidly), and 3-methylindene and benzophenone yield *ωω-diphenyl-3-methylbenzfulvene*, yellow crystals, m. p. 120—121° (*picrate*, pale red needles, m. p. 149—151°), the last condensation being effected by boiling with alcoholic potassium ethoxide for seventeen hours. The last-mentioned benzfulvene is also obtained by boiling a mixture of 3-benzhydrylindene, paraformaldehyde, absolute alcohol, and 28% methyl-alcoholic potassium hydroxide for one hour.

The preceding four benzfulvenes of type II are all intensely yellow, and are reducible by aluminium amalgam and moist ether; the reduction of ωω-diphenyl-3-methylbenzfulvene proceeds very slowly and incompletely, the product being *3-benzhydryl-1-methylindene*, $C_6H_4<{C(CHPh_2) \atop CHMe}>CH$, colourless needles, m. p. 162·5—163·5°.

The groups phenyl, *p*-anisyl, benzhydryl, and furyl in all possible pairs have been systematically introduced into the ω- and the 3-positions in benzfulvene. The case of the pair phenyl and *p*-anisyl has been investigated by Thiele and Merck (*loc. cit.*); both isomerides are known, 3-benzyl-1-*p*-anisylideneindene being the more stable. Other pairs of isomerides which exhibit transformation are the following: 3-Benzhydrylindene and benzaldehyde are condensed by methyl-alcoholic potassium hydroxide, after one day at the ordinary temperature, or after thirty seconds in the boiling solution, yielding *3-benzhydryl-1-benzylideneindene*, pale yellow needles, m. p. 131·5—132·5°. If the boiling is prolonged to five minntes, a difficultly separable mixture of this and its isomeride, *ωω-diphenyl-3-benzylbenzfulvene*, deep yellow, quadratic leaflets, m. p. 130—130·5°, is obtained. The transformation is easily and completely effected by boiling a mixture of 3-benzhydrylindene, benzaldehyde, pyridine, and 28% methyl-alcoholic potassium hydroxide for one minute. This method of preparing ωω-diphenyl-3-benzylbenzfulvene is much to be preferred to that in which 3-benzylindene and benzophenone are condensed by methyl-alcoholic potassium hydroxide, since in the latter considerable quantities of benzhydrol are formed. Thiele and Merck (*loc. cit.*) prepared 3-benzhydryl-1-*p*-anisylideneindene at the ordinary

temperature. It is also obtained at the b. p. after thirty seconds, but after boiling with alkali for one hour in alcoholic or pyridine solution, is transformed into *ωω-diphenyl-3-p-methoxybenzylbenzfulvene*, yellow needles, m. p. 127—128°. The preparation of the two following pairs of isomerides containing furyl and phenyl or *p*-anisyl groups at first presented great difficulty, on account of the extreme ease with which the unstable isomeride is converted into the stable one. *1-Furfurylideneindene* (*ω-furylbenzfulvene*), $C_6H_4<\substack{CH \\ C(:CH\cdot C_4H_3O)}>CH$, yellow needles, m. p. 86—86·5° (*picrate*, red needles, m. p. 103—105°), prepared from indene and furfuraldehyde in boiling methyl-alcoholic potassium hydroxide (five minutes), is reduced by aluminium amalgam and moist ether to *3-furylmethylindene*, $C_6H_4<\substack{CH_2 \\ C(CH_2\cdot C_4H_3O)}>CH$, almost colourless liquid with a pleasant, aromatic odour, b. p. 166—168°/15 mm. From the last compound and benzaldehyde *3-furylmethyl-1-benzylideneindene*, yellow needles, m. p. 93—94·5° (clear at 98°), must be obtained merely by shaking with hot methyl-alcoholic potassium hydroxide and immediately pouring the mixture into water. If the mixture is boiled even for only thirty seconds, the substance is transformed into *1-furfurylidene-3-benzylideneindane*,

$$C_6H_4<\substack{C(:CH\cdot C_4H_3O) \\ C(=\!=CHPh)}>CH_2,$$

faintly yellow needles, m. p. 160·5—161°, which by boiling with methyl-alcoholic potassium hydroxide for four hours is converted into *1-furfurylidene-3-benzylindene*, yellow needles, m. p. 126—127°; the last substance is obtained directly by the condensation of 3-benzylindene and furfuraldehyde. Using *p*-anisaldehyde *in place of benzaldehyde, the following substances are* obtained by methods similar to the preceding: *1-anisylidene-3-furylmethylindene*, yellow leaflets, m. p. 88—89°, *1-anisylidene-3-furfurylideneindane*, yellow needles, m. p. 150—150·5°, and *3-p-methoxybenzyl-1-furfurylideneindene*, golden-yellow leaflets, m. p. 127—128°. The condensation of 3-benzhydrylindene and furfuraldehyde by methyl-alcoholic potassium hydroxide, whether boiled for three seconds or for one hour, yields *3-benzhydryl-1-furfurylideneindene*, yellow needles, m. p. 170—170·5°, which is *not changed by alkali even in the presence of pyridine.* The isomeride was not prepared.

An examination of all the preceding pairs of isomerides shows *that in every transformation the double linking shifts*, so that the partial valencies are balanced as much as possible, and consequently the more saturated system is formed. In the four cases *in which the substituents are a methyl group and an aromatic* group, the more saturated system is formed so easily that the more unsaturated isomeride is unknown. When the substituents are *two aromatic groups, a partial balance of the valencies occurs in* both isomerides, and the transformation is rendered more difficult and leads to the formation of the isomeride in which the exocyclic

double linking is conjugated with the more strongly unsaturated substituent; this isomeride is therefore the more intensely coloured of the pair.

1-*Furfurylidene-3-furylhydroxymethylindene*,

$$C_6H_4<\begin{matrix}C(CH[OH]\cdot C_4H_3O)\\C(:CH\cdot C_4H_3O)\end{matrix}>CH,$$

yellow needles, m. p. 114·5—115°, obtained by condensing indene and furfuraldehyde by means of cold methyl-alcoholic potassium hydroxide for six hours, is reduced by aluminium amalgam and moist ether to 1 : 3-*difurfurylideneindane*,

$$C_6H_4<\begin{matrix}C(:CH\cdot C_4H_3O)\\C(:CH\cdot C_4H_3O)\end{matrix}>CH_2,$$

faintly yellow needles, m. p. 132·5—133·5°, which is also obtained by boiling for one minute with alcoholic alkali 3-*furylmethyl-1-furfurylideneindene*, yellowish-brown needles, m. p. 103—104°, prepared from 3-furylmethylindene and furfuraldehyde.

3-Arylated benzfulvenes containing two aliphatic groups in the ω-positions are quite generally incapable of transformation. ω-*Methyl-ω-ethylbenzfulvene*, prepared by boiling indene and methyl ethyl ketone with alcoholic alkali for five hours, is a faintly yellow oil, b. p. 151—152°/15 mm. (*picrate*, orange needles, m. p. 87·5—88°, sintering at 85°), which is reduced by sodium and absolute alcohol to 3-iso*butylindene*, a colourless oil, b. p. 116—118°/12 mm. The last substance and benzophenone condense when boiled for twenty-three hours with pyridine and alcoholic alkali to form ωω-*diphenyl*-3-iso*butylbenzfulvene*, yellow needles or stout prisms, m. p. 91—92°. 3-*Benzhydryl-ω-methyl-ω-ethylbenzfulvene*, prepared from 3-benzhydrylindene and methyl ethyl ketone and boiling alcoholic alkali (fifteen minutes), is a faintly yellow, crystalline powder, m. p. 149·5—151°. 3-*iso*Propylindene and benzophenone yield ωω-*diphenyl*-3-iso*propylbenzfulvene*, yellow, crystalline powder, m. p. 127—128°. 3-Benzhydrylindene and acetone yield 3-*benzhydryl-ωω-dimethylbenzfulvene*, yellow, crystalline powder, m. p. 174—175°.

The reduction of 3-benzhydryl-1-benzylideneindene and of ωω-diphenyl-3-benzylbenzfulvene by aluminium amalgam and moist ether leads to the same product, namely, a mixture of a *substance*, $C_{29}H_{24}$, hard crystals, m. p. 130—131°, and an isomeric *substance*, slender needles, m. p. 137—138°, which are the two benzylbenzhydrylindenes; also the reduction of ωω-diphenyl-3-*iso*butylbenzfulvene yields a mixture of two isomerides, namely, *benzhydryl*iso*butylindene* I, colourless needles, m. p. 121—123°, and *benzhydryl*iso*butylindene* II, slender needles, m. p. 94—95·5°. The latter is obtained from the former by boiling with alcoholic alkali for thirty minutes, and also from 3-benzhydryl-ω-methyl-ω-ethylbenzfulvene by reduction with sodium and alcohol.

The reduction of benzfulvenes in ethereal solution with platinum-black and hydrogen leads to the formation of indanes. Thus 3-benzhydryl-ωω-dimethylbenzfulvene yields 3-*benzhydryl*-1-iso*propylindane*, slender needles, m. p. 126·5—127·5°, and ωω-di-

phenyl-3-*iso*butylbenzfulvene yields 1-*benzhydryl*-3-iso*butylindane*, colourless crystals, m. p. 104—106°. C. S.

Action of Sulphur on Organic Compounds. I. Hydrocarbons. LUDWIK SZPERL (*Chemik Polski*, 1917, **15**, 10—18; from *Chem. Zentr.*, 1918, i, 908. Compare following abstracts).—A review of the literature of the subject. H. W.

Action of Sulphur on Organic Compounds. II. Diphenylmethane and Fluorene. Dibenzyl. LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski*, 1917, **15**, 19—22; from *Chem. Zentr.*, 1918, i, 908—909. Compare preceding abstract).—Contrary to the statement of Kaufmann, the authors find that diphenyldiphenylene-ethylene, $CPh_2\!:\!C\!<\!\begin{smallmatrix}C_6H_4\\|\\C_6H_4\end{smallmatrix}$, is the main product formed when a mixture of diphenylmethane and fluorene is heated with sulphur until hydrogen sulphide ceases to be evolved, the substance separates from acetone in needles containing acetone of crystallisation, which is lost on exposure to air. It then has m. p. 229—229·5°. Tetraphenylethane, tetraphenylethylene, tetraphenylene-ethane, and tetraphenylene-ethylene are simultaneously produced.

Tetraphenylthiophen, $C_{28}H_{20}S$, m. p. 183—184°, is the sole product of the action of sulphur on dibenzyl at 260°. H. W.

Action of Sulphur on Organic Compounds. III. Benzyl Alcohol, Diphenylcarbinol. LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski*, 1917, **15**, 23—27; from *Chem. Zentr.*, 1918, i, 909. Compare preceding abstracts).—Visible reaction between benzyl alcohol and sulphur commences at about 180°, water, hydrogen sulphide, and benzaldehyde being evolved. The product of the reaction contains, in addition, benzoic acid, tetraphenylthiophen, stilbene, and small quantities of needles, m. p. 127—130°. The main products are tetraphenylthiophen and benzoic acid.

Diphenylcarbinyl ether, $C_{26}H_{22}O$, m. p. 108·5—109°, together with small quantities of benzophenone and possibly traces of diphenylmethane, is produced when diphenylcarbinol is heated with sulphur at 180°, and the action is stopped when water vapour ceases to be evolved. The formation of the ether is attributed to the catalytic action of sulphur on the alcohol. Similarly, benzyl alcohol when heated with 0·1 gram-atom of sulphur gives a 20% yield of dibenzyl ether, b. p. 295—298°. It is therefore to be assumed that the products isolated from the alcohols are due to the action of sulphur on the ethers, and not on the alcohols themselves. H. W.

Action of Sulphur on Organic Compounds. IV. Dibenzyl Ether and Benzhydryl Ether. LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski*, 1917, **15**, 28—33; from *Chem. Zentr.*, 1918, i, 909—910. Compare preceding abstracts).—With the object of verifying the hypothesis that the formation of the corresponding ethers from henzyl alcohol and diphenylcarbinol

is to be attributed to the catalytic action of sulphur, and that other possible admixtures are without influence, the following experiments have been performed. Pure benzyl alcohol was heated at 180° for several hours alone and with intermittent treatment with hydrogen sulphide; the results were negative. Slightly impure diphenylcarbinol (prepared from benzaldehyde and phenyl magnesium bromide and containing traces of magnesium, chlorine, *etc.*) gave after three hours at 150—152° an almost quantitative yield of benzhydryl ether, but the change proceeded less rapidly with a purer material.

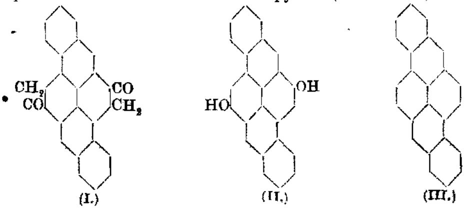
Benzyl ether, when heated with sulphur below 200°, yielded hydrogen sulphide, benzaldehyde, benzoic acid, stilbene, and tetraphenylthiophen. Diphenylcarbinyl ether gave benzophenone and tetraphenylethylene. The reactions occurred, therefore, in precisely the same manner as with the corresponding alcohols; they may be represented by the schemes: $2(PhCH_2)_2O + 2S = 2H_2S + 2C_6H_5{\cdot}CHO + CHPh{:}CHPh$, $2(Ph_2CH)_2O + 2S = 2H_2S + 2COPh_2 + CPh_2{:}CPh_2$. H. W.

Attempted Synthesis of 3 : 4 : 8 : 9-Dibenzopyrene. RICHARD WEITZENBÖCK (*Monatsh.*, 1918, **39**, 307—313).—By the synthetic method already discovered for pyrene (Weitzenböck, A., 1913, i, 259), it should be possible to produce pyrene derivatives containing condensed hydrocarbon nuclei; the paper records an unfinished investigation in this direction.

1 : 1′-Dimethyl-2 : 2′-dinaphthyl, prepared by the action of copper on 2-iodo-1-methylnaphthalene (Scholl, this vol., i, 484), is accompanied by a *substance*, $C_{22}H_{16}$, leaflets, m. p. 314—316°; *picrate*, brick-red needles, m. p. 199—201°. When brominated in boiling nitrobenzene solution, 1 : 1′-dimethyl-2 : 2′-dinaphthyl is converted into 1 : 1′-*dibromomethyl*-2 : 2′-*dinaphthyl*, $C_{22}H_{16}Br_2$, needles, m. p. 200—201°, which reacts with aqueous-alcoholic potassium cyanide, yielding 2 : 2′-*dinaphthylene*-1 : 1′-*diacetonitrile*, crystals, m. p. 264°; this on hydrolysis with alcoholic potassium hydroxide at 150° gives 2 : 2′-*dinaphthylene*-1 : 1′-*diacetic acid*,

$$C_6H_4<\begin{matrix}CH{=\!=\!=}CH\\C(CH_2{\cdot}CO_2H)\end{matrix}>C{-}C<\begin{matrix}CH{=\!=\!=}CH\\C(CH_2{\cdot}CO_2H)\end{matrix}>C_6H_4.$$

From this, by the stages represented by formulæ I and II, it should be possible to obtain 3 : 4 : 8 : 9-dibenzopyrene (formula III).



(I.) (II.) (III.)

In a preliminary investigation with a view to a new pyrene synthesis, *o*-iodophenyldichloropropionic acid, obtained by the action of chlorine on a carbon disulphide solution of *o*-iodocinnamic acid, was steam distilled in the presence of excess of sodium carbonate, with formation of *o-iodostyryl chloride*, $C_6H_4I{\cdot}CH{:}CHCl$, b. p. 151°/24 mm. D. F. T.

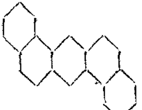
Synthesis of the Isomeric Hydrocarbons 1 : 2 : 5 : 6-Dibenzanthracene and 3 : 4 : 5 : 6 - Dibenzphenanthrene. RICHARD WEITZENBÖCK and ALBERT KLINGLER (*Monatsh.*, 1918, **39**, 315—323. Compare Weitzenböck and Lieb, A., 1912, i, 547). —When heated with *o*-nitrobenzaldehyde in acetic anhydride solution, potassium phenylenediacetate undergoes conversion into *o-nitrobenzylidene*-p-*phenylenediacetic acid*,

$$CO_2H{\cdot}CH_2{\cdot}C_6H_4{\cdot}C(CO_2H){:}CH{\cdot}C_6H_4{\cdot}NO_2,$$

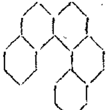
colourless needles, m. p. 236°, which by further treatment can be made to yield *di-o-nitrobenzylidene*-p-*phenylenediacetic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}C(CO_2H){\cdot}C_6H_4{\cdot}C(CO_2H){:}CH{\cdot}C_6H_4{\cdot}NO_2$, pale yellow prisms, m. p. 308° (decomp.). This substance on reduction in ammoniacal solution with ferrous hydroxide gives *di-o-aminobenzylidene*-p-*phenylenediacetic acid*,

$$NH_2{\cdot}C_6H_4{\cdot}CH{:}C(CO_2H){\cdot}C_6H_4{\cdot}C(CO_2H){:}CH{\cdot}C_6H_4{\cdot}NH_2,$$

yellow needles, m. p. near 276°, which by diazotisation and subsequent treatment with copper powder can be made to yield a mixture of 1 : 2 : 5 : 6-dibenzanthracenedicarboxylic acid and 3 : 4 : 5 : 6-dibenzphenanthrenedicarboxylic acid; these were not separated, the mixture being directly converted by heating under reduced pressure into a mixture of the corresponding hydrocarbons, which were then separated by crystallisation from acetic acid. The less soluble 1 : 2 : 5 : 6-*dibenzanthracene* (formula I) forms silvery leaflets, m. p. 262° (*picrate*, $C_{22}H_{14},2C_6H_3O_7N_3$, orange needles, m. p. 214°), gives a red solution with alkaline sodium hyposulphite solution, and is oxidisable by potassium dichromate in acetic acid to 1 : 2 : 5 : 6-*dibenzanthraquinone*, $C_{22}H_{12}O_2$, orange needles, m. p. 248—249°, whilst the more soluble 3 : 4 : 5 : 6-*dibenzphenanthrene* (formula II) forms colourless needles, m. p. 145—146°.



(I.)



(II.)

D. F. T.

Preparation of Hydrogenated Compounds. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P., 305347; from *Chem. Zentr.*, 1918, i, 977).—The process depends on the action of alkali or alkali earth metals and alcohols on isocyclic or heterocyclic bases

in the presence of an inert solvent; the alcohol is preferably added at the same rate as it is used in the reaction. Thus tetrahydro-α-naphthylamine is formed when a solution of α-naphthylamine in alcohol is added to a mixture of solvent naphtha and sodium at a temperature above 130°; with a solvent of lower b. p., such as toluene, dihydro-α-naphthylamine is obtained. 2-Methylquinoline, when hydrogenated at above 130°, yields tetrahydro-2-methylquinoline, which gives a characteristic blood-red coloration with ferric chloride and potassium ferricyanide. The picrate has m. p. 153—154°. H. W.

Phenylpropionamidine. Roland Scholl [with E. Bertsch] (*Monatsh.*, 1918, **39**, 238—240).—Phenylpropionamidine,

NH:CEt·NHPh,

m. p. 72—73° (Michael and Wing, A., 1886, 148, give 68°), is formed when propionitrile is heated with aniline hydrochloride in a sealed tube at 170—180° for twelve hours; *hydrochloride*, hygroscopic; *hydrogen oxalate*, m. p. 141—142°; *picrate*, m. p. 152—153°. D. F. T.

Phenyl and Alkyl Phenyl Esters of Phosphorous Acid. T. Milobendzki and K. Szulgin (*Chemik Polski*, 1917, **15**, 66—75; from *Chem. Zentr.*, 1918, i, 914—915. Compare this vol., i, 477, 478, 479).—The action of alcohols on triphenyl phosphite leads to replacement of the phenyl groups, but isomerisation occurs simultaneously with the formation of phosphinic esters: $P(OPh)_3 + 3PrOH = PPrO(OPr)_2 + 3PhOH$. Diphenyl esters may be obtained by the use of sodium alkyloxides:

$$P(OPh)_3 + PrONa = OPr{\cdot}P(OPh)_2 + PhONa \xrightarrow{HCl\ gas} OH{\cdot}P(OPh)_2 + C_3H_7Cl.$$

Triphenyl phosphite, b. p. 235°/18 mm., is obtained in 91% yield by the gradual addition of phosphorus trichloride to a mixture of phenol and pyridine. It does not react with cold alcohols. Methyl alcohol at 225° transforms it completely into dimethyl methylphosphinate, b. p. 181°/754 mm. *Dipropyl propylphosphinate* (formed, together with small quantities of tripropyl phosphite, in a similar manner) is a colourless liquid, b. p. 126°/18 mm., D_0^{22} 1·0327, D_4^{22} 1·0324. *Tripropyl phosphite* (by action of sodium propoxide [4 parts] and triphenyl phosphite [1 part] in benzene solution) has b. p. 103°/24 mm., whilst *tributyl phosphite* has b. p. 120°/10 mm. The action of sodium propoxide (1 part) on triphenyl phosphite (1 part) leads to the formation of *propyl diphenyl phosphite*, b. p. 203—204°/24 mm., D_0^{19} 1·1153, D_4^{19} 1·1149. *Butyl diphenyl phosphite* has b. p. 198°/12 mm., D_0^{22} 1·0918, D_4^{22} 1·0917. Propyl diphenyl phosphite is obtained in better yield by the gradual addition of diphenylphosphorous chloride, $P(OPh)_2Cl$, to a mixture of propyl alcohol and pyridine; it is slowly hydrolysed by water or alkalis.

Diphenyl phosphite, b. p. 218—219°/25 mm., is prepared by

saturating ice-cold diphenyl propyl phosphite with hydrogen chloride (1 mol.). The alkaline solution of the substance gives with ferric chloride a *precipitate* of the composition (PhO)(FeO)POH [?]. H. W.

***o*-Nitrosophenol. III. Preparation of *o*-Nitrosophenol as a Lecture Experiment [Reagent for Copper].** OSKAR BAUDISCH (*Ber.*, 1918, **51**, 1058—1059. Compare A., 1916, i, 33).—A solution containing *o*-nitrosophenol may be quickly prepared as follows: a crystal or two of *o*-nitrophenol is dissolved in a few drops of hot acetic acid, cooled, diluted a little, covered with light petroleum, and shaken with a trace of zinc dust. The aqueous layer becomes pink owing to the formation of the zinc salt of *o*-nitrosophenol, but the free reagent is chiefly contained in the supernatant, green layer. If this solution is shaken with a trace of a copper salt, the petroleum becomes colourless and the aqueous layer deep red. This test for copper is said to be more sensitive than the ferrocyanide reaction. J. C. W.

Preparation of Picramic Acid. GRETE EGERER (*J. Biol. Chem.*, 1918, **35**, 565—566).—Finely powdered picric acid (20 grams) is dissolved in 300 c.c. of alcohol, and 125 c.c. of ammonia (0·880) are added. After cooling to 30°, hydrogen sulphide is passed in rapidly, so that the temperature rises to 50—55° in fifteen minutes. The flask is then cooled in ice, while the stream of hydrogen sulphide is maintained for forty-five minutes. Crystals of ammonium picramate are deposited, and are collected and decomposed by the addition of 60 c.c. of acetic acid (1 part of glacial acid to 4 parts of water). After vigorous stirring, the picramic acid is collected, washed with a little water, and recrystallised from boiling water. Yield, 75 to 80% of the theoretical. H. W. B.

Preparation of Derivatives of *p*-Aminophenol. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 116920, 1917; A., 1901, i, 533).—*p-Aminophenyl allyl ether* (Spiegel & Sabbath) is poisonous, but its acyl derivatives are not poisonous in therapeutic doses, and possess narcotic, sedative, and anti-neuralgic properties. *p*-Acetylaminophenyl allyl ether forms lustrous leaflets, m. p. 94°, readily soluble in alcohol, ether, and acetone, and somewhat readily so in hot water. The *lactyl* derivative forms lustrous leaflets, m. p. 87°, readily soluble in alcohol, ether, and benzene, and somewhat readily so in hot water; the iso*valeryl* derivative forms small, lustrous needles, m. p. 95°, and the *a-bromoisovaleryl* derivative lustrous leaflets, m. p. 131°. A. S.

Compounds of *p*-Phenetidine. L. REUTTER (*Schweiz. Apoth.-Zeit.*, 1917, **55**, 692; from *Chem. Zentr.*, 1918, i, 825—826).—Di-*p*-phenetylthiocarbamide, lead carbonate, alcohol, and aqueous potassium cyanate reacting first in the cold and then at 45° yield the *nitrile*, $OEt\cdot C_6H_4\cdot NH\cdot C(CN):N\cdot C_6H_4\cdot OEt$, yellow crystals,

m. p. 104°, which is converted into a *substance*, $C_{18}H_{21}O_2N_3S$, yellow prisms, m. p. 124°, by shaking with yellow ammonium sulphide for three days, and finally warming at 30—35°, and into a *substance*, $C_{18}H_{22}O_3N_3Cl$, whitish-yellow crystals, m. p. 220°, by dissolution in concentrated hydrochloric acid on the water-bath.

C. S.

Preparation of Guaiacol. ERNST H. ZOLLINGER and HERMANN RÖHLING (D.R.-P., 305281; from *Chem. Zentr.*, 1918, i, 977).—A weak base such as sodium carbonate or sodium hydrogen carbonate is gradually added to a mixture of catechol with the alkali or alkali earth salts of methylsulphuric acid in the presence of veratrole as diluent at 160—180°; the yield is more than 85% of that theoretically possible.

H. W.

Polyhydric Mercaptans of the Benzene Series. VI. Homologous Dithiolbenzenes. J. POLLAK and B. SCHADLER (*Monatsh.*, 1918, **39**, 129—148. Compare Pollak and others, A., 1915, i, 529; 1914, i, 39; 1910, i, 734; 1909, i, 791).—By treatment with fuming sulphuric acid, *m*-xylene was converted into a mixture of disulphonic acids, from which by the action of phosphorus pentachloride a mixture of the corresponding *m*-xylene-2:4-disulphonyl chloride and *m*-xylene-2:5-disulphonyl chloride was obtained (compare Pfannenstill, A., 1892, 1340). The crystalline 2:4-disulphonyl chloride on reduction with tin and hydrochloric acid gives 2:4-*dithiol*-m-*xylene*, $C_6H_2Me_2(SH)_2$, leaflets, m. p. 123—125° (*acetyl* derivative, $C_6H_2Me_2(SAc)_2$, leaflets, m. p. 76·5—79°), which reacts with chloroacetic acid and ethyl chloroformate respectively in alkaline solution, yielding m-*xylene-2:4-dithiolacetic acid*, $C_6H_2Me_2(S{\cdot}CH_2{\cdot}CO_2H)_2$, colourless, stellar aggregates, m. p. 185—189°, and 2:4-*diethylthiocarbonato*-m-*xylene*,

$$C_6H_2Me_2(S{\cdot}CO_2Et)_2,$$

long needles, m. p. 61—63°, and is converted by aqueous hydrogen peroxide into a *substance*, $(C_6H_2Me_2S_2)_x$, needles, m. p. 252—255°; with picryl chloride, the mercaptan reacts, producing 2:4-*dipicrylthiol*-m-*xylene*, $C_6H_2Me_2[S{\cdot}C_6H_2(NO_2)_3]_2$, orange-coloured needles with $1C_6H_6$, m. p. 258—259·5°. Treatment with methyl sulphate in the presence of alkali converts the mercaptan into 2:4-*dimethylthiol*-m-*xylene*, $C_6H_2Me_2(SMe)_2$, needles, m. p. 83—84·5°, which reacts with chlorine, yielding a *substance*, $C_{10}H_{11}S_2Cl_3$, and with bromine in chloroform solution, giving an *additive* compound, $C_6H_2Me_2(SMe)_2Br_2$, deep red needles, decomp. 99—102°; this regenerates the parent dimethylthiolxylene when shaken in chloroform solution with aqueous sodium hydrogen sulphite. Oxidation with aqueous potassium permanganate converts the dimethylthiolxylene into the *disulphone*, $C_6H_2Me_2(SO_2Me)_2$, needles, m. p. 187—188°.

In a similar manner, the isomeric oily *m*-xylene-2:5-disulphonyl chloride can be reduced to an oily 2:5-*dithiol*-*m*-*xylene*, b. p. 142—144°/9 mm., which reacts with chloroacetic acid in alkaline

solution, giving m-*xylene*-2:5-*dithiolacetic acid*, stellar aggregates, m. p. 158—161°, and with picryl chloride forming 2:5-*dipicrylthiol*-m-*xylene*, crystals, m. p. 211—213°. The 2:5-*dimethylthiol*-m-*xylene*, b. p. 167—169°/14 mm., obtained by methylation with methyl sulphate, undergoes substitution when treated in chloroform solution with bromine, yielding a *bromo*-derivative,

$C_6HBrMe_2(SMe)_2$,

crystalline scales, m. p. 122—123°. The unexpected greater ease of bromination of this dimethylthiolxylene as compared with its 2:4-isomeride led to a doubt as to whether the relative structures of these substances are really as assumed above (compare Zincke and Krüger, A., 1913, i, 44), but an attempt to decide this matter by heating the 2:4-disulphonyl chloride with thionyl chloride in the hope of replacing the $-SO_2Cl$ groups by chlorine atoms was unsuccessful, the product being a *substance*, $C_8H_4O_2Cl_4$, crystalline scales, m. p. 76—77°, possibly 2:4-dichloro-*m*-phthaloyl chloride. A somewhat similar reaction to this was observed between 1:3-dimethoxybenzene-4:6-disulphonyl chloride and thionyl chloride at 170°, the product being a substance, $C_8H_6O_2Cl_4$, needles, m. p. 95—98°, possibly of the structure $C_6H_2Cl_2(O\cdot CH_2Cl)_2$ (compare Meyer, A., 1916, i, 134).

2:6(?)-*Dithiol*-p-*xylene*, b. p. 145·5°/11·5 mm. (*diacetyl* derivative, needles, m. p. 79·5—82·5°; p-*xylene*-2:6-*dithiolacetic acid* derivative, needles, m. p. 170·5—174·5°; *dipicryl* derivative, yellow, crystalline solid, m. p. 251—255°; *dimethyl* derivative, needles, m. p. 92—94°), is obtainable from *p*-xylene through the disulphonyl chloride. D. F. T.

Polyhydric Mercaptans of the Benzene Series. VII. Substituted Thiolbenzenes. J. Pollak, Luzie von Fiedler, and Heinrich Roth (*Monatsh.*, 1918, **39**, 179—200. Compare Pollak and Schadler, preceding abstract).—The effect of the introduction of a methyl group on the m. p. of the polyhydric mercaptans is rather irregular; thus 1:3-dithiolbenzene and 2:4-dithiol-*m*-xylene have m. p. 25° and 121° respectively (*loc. cit.*), whereas the substitution of a methyl group into the nucleus of trithiolbenzene causes a small depression of the m. p. Further compounds were therefore prepared with the view of investigating the influence of such substitution more widely, but no general regularities were observed either with the m.p.'s or b.p.'s.

1-*Ethylbenzene*-2:4-*disulphonic acid* (*barium* salt, crystalline with $2\frac{1}{2}H_2O$), obtained by the action of fuming sulphuric acid on benzene, was converted into the corresponding acid *chloride*, $C_6H_3Et(SO_2Cl)_2$, by the action of phosphorus pentachloride on its *sodium* salt at 140—150°; the corresponding 1-*ethylbenzene*-2:4-*disulphonamide*, $C_6H_3Et(SO_2\cdot NH_2)_2$, m. p. 186—190°, was obtained from the chloride by the action of warm aqueous ammonia. On reduction with tin and hydrochloric acid, the acid chloride is converted into 2:4-*dithiol*-1-*ethylbenzene*, $C_6H_3Et(SH)_2$, an oil, b. p. 150—152°/18—20 mm., which reacts with alkaline methyl sulphate,

yielding 2:4-*dimethylthiol*-1-*ethylbenzene*, $C_6H_3Et(SMe)_2$, a pale yellow oil, b. p. 171—173°/14 mm., whilst with ethyl chloroformate and methyl chloroformate in the presence of alkali the products are colourless 2:4-*diethylthiocarbonato*-1-*ethylbenzene*, $C_6H_3Et(S{\cdot}CO_2Et)_2$, b. p. 224—226°/14 mm., and the corresponding 2:4-*methyldithiocarbonato*-1-*ethyl benzene*, $C_6H_3Et(S{\cdot}CO_2Me)_2$, a colourless oil, b. p. 217—220°/18 mm., respectively; the dithiol compound also reacts with chloroacetic acid in the presence of alkali and with picryl chloride, yielding, respectively, 1-*ethylbenzene*-2:4-*dithiolacetic acid*, $C_6H_3Et(S{\cdot}CH_2{\cdot}CO_2H)_2$, colourless crystals, m. p. 137—140°, and 2:4-*dipicrylthiol*-1-*ethylbenzene*, $C_6H_3Et[S{\cdot}C_6H_2(NO_2)_3]_2$, yellow needles, m. p. 197·5—199°; when heated with sodium acetate and acetic anhydride, the dithiol compound is converted into the *diacetyl* derivative, $C_6H_3Et(SAc)_2$, b. p. 218—220°/18 mm., and in the presence of alcoholic ammonia is oxidised by concentrated hydrogen peroxide with formation of a *substance*, $(C_6H_3EtS_2)_n$. Nitric acid in the cold converts 2:4-dimethylthiol-1-ethylbenzene into 5-*nitro*-2:4-*dimethylthiol*-1-*ethylbenzene*, $NO_2{\cdot}C_6H_2Et(SMe)_2$, yellow, silky needles, m. p. 117—118°, whereas fuming nitric acid effects an oxidation to a *monosulphoxide* of the last product, $NO_2{\cdot}C_6H_2Et(SMe){\cdot}SMeO$, yellow, silky needles, m. p. 119·5—120·5°.

In a similar manner to the preceding, 1-ethylbenzene-4-sulphonyl chloride was made to yield 4-*thiol*-1-*ethylbenzene*, $C_6H_4Et{\cdot}SH$, b. p. 91—93°/12—13 mm. (*acetyl* derivative, $C_6H_4Et{\cdot}SAc$, b. p. 136·5—140°/13—14 mm.), which in alkaline solution reacts with chloroacetic acid, giving 1-*ethylbenzene*-4-*thiolacetic acid*, $C_6H_4Et{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, colourless, silky needles, m. p. 61—67°, and in alcoholic solution with picryl chloride, forming 4-*picrylthiol*-1-*ethylbenzene*, $C_6H_4Et{\cdot}S{\cdot}C_6H_2(NO_2)_3$, deep yellow, silky needles, m. p. 113·5—116°.

By treating phenol with fuming sulphuric acid, a mixture of sulphonic acids can be obtained which, on conversion into the corresponding sodium or potassium salts and heating with phosphorus pentachloride at 140—150°, yields a more soluble (in ether) 4-*chlorobenzene*-1:3-*disulphonyl chloride*, $C_6H_3Cl(SO_2Cl)_2$, needles, m. p. 87—88°, and a less soluble 2-*chlorobenzene*-1:3:5-*trisulphonyl chloride*, $C_6H_2Cl(SO_2Cl)_3$, pale yellow needles, m. p. 170—171°. The former product on reduction with tin and hydrochloric acid gives 4-*chloro*-1:3-*dithiolbenzene*, $C_6H_3Cl(SH)_2$, a pale yellow liquid, b. p. 145—146°/13—14 mm. (*acetyl* derivative, $C_6H_3Cl(SAc)_2$, b. p. 214—217°/19 mm; *picryl* derivative, $C_6H_3Cl[S{\cdot}C_6H_2(NO_2)_3]_2$, golden-yellow platelets, m. p. 201—204°; *dimethyl* derivative, $C_6H_3Cl(SMe)_2$, pale yellow oil, b. p. 177—179°/18 mm.; 4-*chlorobenzene*-1:3-*dithiolacetic acid*,

$$C_6H_3Cl(S{\cdot}CH_2{\cdot}CO_2H)_2,$$

silky needles, m. p. 159—160°; the reaction with ethyl chlorocarbonate followed an unusual course, the product under normal conditions consisting of 4-*chloro*-3(?)-*thiol*-1(?)-*ethylthiocarbonatobenzene*, $SH{\cdot}C_6H_3Cl{\cdot}S{\cdot}CO_2Et$, b. p. 204°/18 mm., the completely

substituted 4-*chloro*-1 : 3-*diethylthiocarbonatobenzene*,

$$C_6H_3Cl(S\cdot CO_2Et)_2,$$

needles, m. p. 48—49°, being obtained only with the use of an excess of ethyl chlorocarbonate. The reduction of 2-chlorobenzene-1 : 3 : 5-trisulphonyl chloride gave 2-*chloro*-1 : 3 : 5-*trithiolbenzene*, $C_6H_2Cl(SH)_3$, yellow crystals, m. p. 64—67°; *methyl* derivative, $C_6H_2Cl(SMe)_3$, needles, m. p. 92—94°; 2-*chlorobenzene*-1 : 3 : 5-*trithiolacetic acid*, $C_6H_2Cl(S\cdot CH_2\cdot CO_2H)_3$, colourless needles, m. p. 199—200°. D. F. T.

Energetic Oxidation of Cholesterol by Nitric Acid. ADOLF WINDAUS (*Zeitsch. physiol. Chem.*, 1918, **102**, 160—165).—The following compounds have been recognised among the products of the oxidation of cholesterol by nitric acid: dinitro*iso*propane and acetic, succinic, methylsuccinic, and α-methylglutaric acids. Acetone, hydroxy*iso*butyric acid, methyl *iso*hexyl ketone, and octane have previously been obtained, and the author points out that all these substances may be regarded as derived from an *iso*octyl side-chain in cholesterol. On this assumption, cholesterol may be represented by the formula

```
           CHMe·CH2·CH2
            |       |
      CH2·CH——————CH·CH·CH2·CHMe·[CH2]3·CHMe2 .
       |           |
  CH2·CH——————CH·CH·CH2
  |              |   |
  CH2·CH(OH)·CH·CH:CH
```

H. W. B.

[Preparation of β-Diethylamino-α-phenylpropyl Benzoate and β-Ethylamino-α-phenylpropyl Benzoate.] NAGAYOSHI NAGAI (Brit. Pat. 117486, 1917).—The preparation of two new bases possessing local anæsthetic properties from β-amino-α-phenylpropanol ("mydriatin," Jap. Pat. 27056) is described. Mydriatin is converted into a mixture of its mono- and di-ethyl derivatives by treatment with an ethyl haloid, and the ethyl derivatives are dissolved in ether and benzoylated. The ethereal solution of the benzoyl compounds is shaken with dilute hydrochloric acid, and the aqueous and ethereal layers are separated. From the aqueous layer by evaporation under diminished pressure, β-*diethylamino*-α-*phenylpropyl benzoate* ("*allocain S*"), $NEt_2\cdot CHMe\cdot CHPh\cdot OBz$, is obtained as hydrochloride in the form of a colourless, transparent, vitreous mass. The ethereal solution contains *N*-benzoylethylmydriatin. It is evaporated, the residue heated with 30% hydrochloric acid, diluted, filtered, shaken with ether, and the separated aqueous layer filtered and evaporated, whereon β-*ethylamino*-α-*phenylpropyl benzoate hydrochloride* ("*allocain A*"),

$$NHEt\cdot CHMe\cdot CHPh\cdot OBz,HCl,$$

separates in flat needles. It is stated that benzoic esters of mono- and di-alkyl or mono- and di-aryl derivatives of mydriatin, and benzoic esters of aminophenyl alcohols homologous to mydriatin

and of their alkyl or aryl derivatives, all possess more or less marked anæsthetic properties. A. S.

Coloured Acid Additive Products of Unsaturated Ketones. FRITZ STRAUS [with HUGO BLANKENHORN] (*Annalen*, 1918, **415**, 232—256).—Mylo has shown (A., 1912, i, 4) that the acetals of aldehydes react with phosphorus pentachloride, thionyl chloride, *etc.*, *an alkyloxy-group being replaced by a chlorine atom.* It is now shown that the acetals of certain unsaturated ketones in benzene solution react with hydrogen chloride or, better, phosphorus pentachloride (1 mol.) in the same way; the products are isolated in the form of the yellow or orange-red complex compound with phosphorus pentachloride or mercuric chloride. Thus the acetal of phenyl cinnamylidene methyl ketone in benzene solution is treated with phosphorus pentachloride (1 mol.) dissolved in the same solvent, and to the cooled, clear, faintly coloured solution is added drop by drop, with complete exclusion of moisture, a solution of mercuric chloride in dry ether, whereby the additive compound, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CPhCl{\cdot}OMe,HgCl_2$, m. p. about 110° (decomp.), is precipitated as a red oil, which rapidly solidifies and becomes crystalline. In a similar way, the *acetal* of phenyl styryl ketone, $CHPh{:}CH{\cdot}CPh(OMe)_2$, colourless needles, m. p. 46—46·5°, yields the *substance*, $CHPh{:}CH{\cdot}CPhCl{\cdot}OMe,HgCl_2$, yellow crystals, m. p. about 100° (decomp.), the *acetal* of *pp′*-dimethoxybenzophenone, colourless needles, m. p. 107—108°, yields the *substance*, $OMe{\cdot}CCl(C_6H_4{\cdot}OMe)_2,HgCl_2$, yellow, apparently amorphous powder, and the acetal of benzophenone yields the *substance*, $2CPh_2Cl{\cdot}OMe,5HgCl_2$, almost colourless needles. These substances are converted into the original ketones by hydroxylic solvents, into the original acetals by alcoholic sodium methoxide, and evolve methyl chloride when heated.

The bearing of the preceding substances on the constitution of the coloured acid additive compounds of the ketones is discussed.

The following substances are described: p-*chlorophenyl* p-*methoxystyryl ketone*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4Cl$, yellow needles, m. p. 121—122°, prepared from anisaldehyde and *p*-chloroacetophenone in aqueous alcohol containing about 0·5% of sodium hydroxide; p-*anisyl* p-*chlorostyryl ketone*, pale yellow crystals, m. p. 130—131°; p-*anisyl* p-*chlorocinnamylidenemethyl ketone*, yellow needles, m. p. 140°; p-*chlorophenyl* p-*methoxycinnamylidenemethyl ketone*, golden-yellow needles, m. p. 156°; and p-*chlorodistyryl ketone*, pale yellow needles, m. p. 134°. C. S.

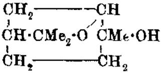
The Quinonoid Oxidation Product of Methylene-di-β-naphthol. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1918, **39**, 299—306).—The yellow quinonoid oxidation product of methylenedi-β-naphthol was regarded by Abel (A., 1893, i, 172) as having the peroxide structure, $C_{10}H_6{<}{}^{CH_2}_{O_2}{>}C_{10}H_6$, but the *o*-quinonoid formula, $CH{\ll}{}^{C_6H_4\text{———}}_{CH\cdot CO}{>}C{:}CH{\cdot}CH{<}{}^{C_6H_4\text{———}}_{CO\cdot CH}{\gg}CH$, is

now proposed. This structure is in accordance with the formation of a *phenylhydrazone*, $C_{27}H_{20}ON_2$, orange-red needles, m. p. 153—156°, only the orthoquinonoid carbonyl group reacting with the usual reagents for ketonic substances; the phenylhydrazone on reduction with zinc and alcoholic acetic acid yields a *dihydro-derivative*, $C_{27}H_{22}ON_2$, a colourless powder, m. p. 133—136°; this derivative is probably a hydrazo-compound, whilst the parent phenylhydrazone is of azo-structure. With magnesium methyl iodide, the quinonoid compound reacts, forming a *substance*, $C_{22}H_{18}O_2$, probably $CH{<}{\genfrac{}{}{0pt}{}{C_6H_4\text{———————}}{CH\cdot CMe(OH)}}{>}C{:}CH\cdot CH{<}{\genfrac{}{}{0pt}{}{C_6H_4\text{——}}{CO\cdot CH}}{>}CH$ needles, m. p. 135—145°, and with magnesium phenyl bromide an analogous derivative, $C_{27}H_{20}O_2$, probably

$$CH{<}{\genfrac{}{}{0pt}{}{C_6H_4\text{———————}}{CH\cdot CPh(OH)}}{>}CH{:}CH\cdot CH{<}{\genfrac{}{}{0pt}{}{C_6H_4\text{——}}{CO\cdot CH}}{>}CH,$$

prisms, m. p. 130—170°, is obtained. Methyl sulphate converts methylenedi-β-naphthol into the *dimethyl* ether, $C_{23}H_{20}O_2$, leaflets, m. p. 144—147°. D. F. T.

***cis-trans*-Isomerism in the Terpene Series. Addition of Hypochlorous Acid to Terpineol.** K. SLAWIŃSKI (*Chemik Polski*, 1917, **15**, 97—105; from *Chem. Zentr.*, 1918, i, 920—921).—Terpineol dissolved in acetic acid was treated with sodium hypochlorite solution (1%); the product could be separated by fractional crystallisation into two portions: (1) m. p. 114—115°, b. p. 162—165°/15 mm., and (2) m. p. 60—80°, b. p. 125—155°, both of which consisted of the chlorohydrin of menthane-1:2:8-triol. The crude substance was treated with potassium hydroxide (20%) and the product separated into a liquid and a solid portion (m. p. *118—118·5°*). The former, on distillation, yielded small quantities of pinol and pinol hydrate (annexed formula), which could only be derived from the *cis*-chlorohydrin of menthane-1:2:8-triol. From the fraction, b. p. 175—180°/13 mm., it was found possible to isolate *cis*-menthane-1:2:8-triol, m. p. 118—118·5°. The chlorohydrin of menthanetriol of m. p. 114—115° yielded almost exclusively pinol hydrate when treated with potassium hydroxide (20%), so that the chlorine atom must be attached to the carbon atom in position 6. From the mixture of chlorohydrins, m. p. 60—80°, only small amounts of the menthanetriol, m. p. 116—117·5°, could be isolated. The glycerol compound is therefore formed from the chlorohydrin of lower m. p. H. W.



Constituents of Resins. II. Constituents of Sumatra Gum Benzoin. HANS LIEB and ALOIS ZINKE (*Monatsh.*, 1918, **39**, 219—230).—Unlike Siamese gum benzoin, Sumatra gum benzoin dissolves completely in hot dilute aqueous sodium hydroxide; the resulting solution, on boiling, deposits the *sodium* salt of l-*benzoresinol*,

m. p. 339—341°, $[\alpha]_D^{?}$ −12·88°, probably of the composition $C_{29}H_{44}O_4$. The mother liquors on the addition of a little ether deposit the *sodium* salt (needles with $4H_2O$) of d-*sumaresinol*, $C_{30}H_{48}O_4,H_2O$, m. p. 298—299°, $[\alpha]_D^{20}$ +51·60° (*methyl* ether, crystals, m. p. 215—216°; *ethyl* ether, needles, m. p. 207—208°), isomeric with siaresinol (this vol., i, 398). The benzoresinol of Lüdy (A., 1893, i, 480, 666) was probably a mixture of *d*-sumaresinol with *l*-benzoresinol. D. F. T.

Vulcanisation without Sulphur by Ostromyslenski's Method. E. Bunschoten (*Kolloid Zeitsch.*, 1918, **23**, [i], 25—31).—Nitrobenzene and *m*-dinitrobenzene alone have little vulcanising action on rubber, and such organic accelerators as *p*-nitrosodimethylaniline have no effect. Metallic oxides, however, act as strong catalysts, particularly lead oxide, which was used for all the experiments recorded. The rate of vulcanisation by *m*-dinitrobenzene depends on the sample of rubber used, and is increased by increasing the amount of catalyst or by increasing the temperature within the limits studied, 137—157°. The optimum time of heating varies as the other factors are varied, but if it is exceeded, the physical properties of the product deteriorate. Samples of rubber vulcanised with dinitrobenzene rapidly deteriorate, and white crystals of unchanged dinitrobenzene make their appearance on the surface.

The viscosity of benzene solutions of rubber is increased by addition of dinitrobenzene in the dark, particularly at high temperatures, but in the light the viscosity rapidly falls off. The opinion is expressed that the vulcanising action of such substances as *m*-dinitrobenzene is due to acceleration of polymerisation of the rubber. Sulphur acts in the same manner, but at the same time enters into combination with the rubber.

When rubber is heated with such inorganic oxidising agents as potassium permanganate, persulphate, dichromate, chlorate, nitrate, arsenic acid, bleaching powder, or manganese dioxide, incipient vulcanisation sets in, but the product is still soluble in benzene after long standing. [See also *J. Soc. Chem. Ind.*, 665A.]

E. H. R.

Scoparin. J. Herzig and Gertrud Tiring (*Monatsh.*, 1918, **39**, 253—267).—Goldschmiedt and von Hemmelmayr (A., 1893, i, 601; 1894, i, 542) have shown that scoparin, obtained from *Spartium scoparium*, contains a methoxyl group and six hydroxyl radicles, and attributed to the substance the formula $C_{20}H_{20}O_{10}$; it was found possible to alkylate only one hydroxyl radicle. By using diazomethane, however, it is possible to obtain a *dimethyl* derivative (*trimethyl*nor*scoparin*), $C_{24}H_{28}O_{12}$, yellow crystals, m. p. 260—265° (decomp.), and a *trimethyl* derivative (*tetramethyl*nor*scoparin*), $C_{25}H_{30}O_{12}$, yellow crystals, m. p. 220—238°, together with an amorphous *substance*. With methyl iodide and silver

*oxide, it is possible to convert scoparin into a crystalline octamethyl*norscoparin, $C_{21}H_{12}O_3(OMe)_8$, *m. p. 120—130°, with* subsequent resolidification and m. p. 229—233°. The composition of these substances, as also that of acetylscoparin, renders it probable that the molecular formula of scoparin is not $C_{20}H_{20}O_{10}$, but $C_{22}H_{22}O_{11}$ (compare also Stenhouse, *Annalen*, 1851, **78**, 15.)

D. F. T.

Synthesis of Alcohols in the Thiophen Series. V. Thomas and V. Couderc (*Bull. Soc. chim.*, 1918, [iv], **23**, 326—328).—Magnesium thienyl iodide reacts with ketones, giving thiophenic alcohols, of which the following have been prepared.

Diphenylthienylcarbinol, $HO\cdot CPh_2\cdot C_4H_3S$, which apparently condenses with aniline hydrochloride, giving a *compound*, colourless leaflets.

Phenyldithienylcarbinol, $HO\cdot CPh(C_4H_3S)_2$, m. p. 90°. With benzil, a *compound* [*thienylphenylbenzoin* ?,

$C_4H_3S\cdot CPh(OH)\cdot COPh$],

m. p. 56°, was obtained.

W. G.

Eserine (Physostigmine). J. Herzig and Hans Lieb (*Monatsh.*, 1918, **39**, 285—292).—The ordinary method for the determination of imino-methyl in eserine gives a result indicating the presence of two such groups, whereas the compound obtained after the removal of two methyl radicles, when examined by the micro-method, shows the presence of a third methyl group (Herzig and Meyer, this vol., i, 383; Straus, A., 1914, i, 78; 1915, i, 448); eseroline, when examined by the micro-method, also gives results almost twice as high for imino-methyl as by the macro-method (Straus, A., 1915, i, 448). This difference appears to be due to the larger proportion of hydriodic acid used in the micro-method, and if in the macro-method only 0·1 gram of eserine is taken to 20 c.c. of hydriodic acid, the result agrees with the presence of three imino-methyl groups. The reason of this peculiarity of eserine is at present undecided, although the possibility that the third and resistant radicle is an ethyl group, and not a methyl, receives some support from the behaviour of eserine when examined by Kirpal and Bühn's method for methyl determination (A., 1914, ii, 497; 1916, ii, 154).

D. F. T.

The Alkaloids of the Calabar Bean. VII. Degradation by successive Iodomethylations of the Nuclei of Eserine and Geneserine. Max Polonovski and Michel Polonovski (*Bull. Soc. chim.*, 1918, [iv], **23**, 335—356. Compare A., 1915, i, 891, 892).—Eserethole methiodide (*loc. cit.*), when decomposed in aqueous solution with sodium carbonate, yields *eseretholemethine*, prisms, m. p. 80°, $[\alpha]_D$ +10°, which gives a *hydriodide*, m. p. 170°, a *hydrochloride*, and a *zincochloride*, m. p. 193°. It is a tertiary base and gives a quaternary *methiodide*, m. p. 100°, $[\alpha]_D$ −11·8°, which when decomposed with aqueous potassium hydroxide yields

trimethylamine and a new base, *etheserolene*, $C_{12}H_{12}N \cdot OEt$, an oil, giving an oily *bromo*-derivative and a crystalline *nitro*-derivative.

With methyl iodide, geneserine gives three compounds, one of which, m. p. 215° (*loc. cit.*), previously described as a methiodide, is really *ψ-geneserinemethine hydriodide*, from which the free *base* is obtained as an uncrystallisable syrup, giving a *methiodide*, m. p. 160° (decomp.), $[\alpha]_D -15°$. This methiodide is also one of the products of iodomethylation of geneserine, and when decomposed by alkalis yields methylamine and *ψ-geneserolenemethine methiodide*, m. p. 261°. The hydriodide, m. p. 215°, described above, when saponified by alkalis, yields *ψ-geneserolenemethine*, m. p. 171°, $[\alpha]_D -46°$, giving a *hydriodide*, m. p. 234°. With ethyl toluenesulphonate, it yields *ψ-geneseretholemethine*, and on acetylation gives *acetylgeneserolenemethine*, of which the *methiodide* has m. p. 175°. The methiodides of *ψ*-geneserinemethine or *ψ*-geneserolenemethine when treated with sodium hydroxide yield *ψ-geneserolene*, $HO \cdot C_{12}H_{12}ON$, m. p. 215°.

Eserine methiodide is converted by the action of hydrogen peroxide into *ψ*-geneserinemethine, and, similarly, eserethole yields *ψ-geneseretholemethine*, giving a *hydriodide*, m. p. 212°, and a *methiodide*, m. p. 130—140°. W. G.

The Alkaloids of the Calabar Bean. VIII. Hydrogenation in the Eserine, Geneserine, and ψ-Geneserine Series. MAX POLONOVSKI (*Bull. Soc. chim.*, 1918, [iv], **23**, 356—361).—Eserine and a number of its derivatives, when reduced by zinc and hydrochloric acid, yield dihydro-derivatives, the following being described.

Neither *dihydroeserine* nor its salts crystallise readily, but a *picrate*, m. p. 100°, was obtained.

Dihydroeseroline, m. p. 140°, gave a *picrate* and a *zincochloride*, m. p. 194°, $[\alpha]_D -95°$.

Dihydroeserethole, an oil, gave a *zincochloride*, m. p. 252°.

Dihydroeseretholemethine, an oil, gave a *zincochloride*, m. p. 242°, and a *methiodide*, m. p. 127°.

Geneserine and its derivatives on reduction gave, first, the corresponding eserine derivatives, and then their dihydro-derivatives.

Eserine methiodide when reduced by zinc and hydrochloric acid in alcoholic solution gave *dihydroeserinemethine*, m. p. 125°, $[\alpha]_D +11°$, which gave a *zincochloride*, m. p. 160°, and a *methiodide*. Eseroline methiodide similarly gave *dihydroeserolinemethine*, m. p. 128—129°. W. G.

Dihydrophenazine and Dihydroacridine. ROLAND SCHOLL [with W. NEUBERGER] (*Monatsh.*, 1918, **39**, 238).—Dihydrophenazine and dihydroacridine are formed when phenazine and acridine, respectively, in hot alcoholic solution are gradually introduced into an aqueous-alcoholic alkaline solution of sodium hyposulphite. D. F. T.

Tetramethyl - 3 : 3′ - diaminodiphenylmethane. ROLAND SCHOLL [with JOS. LENKO] (*Monatsh.*, 1918, **39**, 236—237).—When heated with methyl iodide and methyl alcohol at 140—150°, 3 : 3′-diaminodiphenylmethane is converted into the *methiodide*, $C_{19}H_{28}N_2I_2$, needles, m. p. 165°, of *tetramethyl*-3 : 3′-*diaminodiphenylmethane*, $C_{17}H_{22}N_2$, the oily, free base being obtainable by heating the methiodide with soda-lime in an atmosphere of hydrogen or with concentrated aqueous ammonia in a sealed tube at 180—190°. D. F. T.

Hydrazino-acids. I. AUGUST DARAPSKY (*J. pr. Chem.*, 1917, [ii], **96**, 251—327).—This communication opens with a general review of the subject and a theoretical discussion of the new results, which are grouped under three headings.

I. REDUCTION OF THE HYDRAZONE OF PYRUVIC ACID AND THE HYDRAZONE AND AZINE OF PHENYLGLYOXYLIC ACID, pp. 273—280 [with MORESHWAR PRABHAKAR].—The hydrazine salt of pyruvic acid hydrazone, $NH_2 \cdot N{:}CMe \cdot CO_2H,N_2H_4$ (Curtius and Lang, A., 1891, 452), is reduced by means of sodium amalgam, the product is evaporated to dryness with hydrochloric acid, and then esterified, when the *hydrochloride* of *ethyl* α-*hydrazinopropionate*,

$$CO_2Et \cdot CHMe \cdot N_2H_3,HCl,$$

is obtained in white leaflets, m. p. 108—110° (decomp.). This is identified by conversion into the free acid and its benzylidene compound (Traube and Longinescu, A., 1896, i, 340; Thiele and Bailey, A., 1899, i, 169).

Phenylglyoxylic acid, which is conveniently prepared by oxidising mandelic acid with alkaline permanganate, reacts with alcoholic hydrazine hydrate to give the *hydrazine* salt of *phenylglyoxylic acid hydrazone*, $NH_2 \cdot N{:}CPh \cdot CO_2H,N_2H_4$, which crystallises in long needles, m. p. 160—161°, and yields hydrazinophenylacetic acid on reduction with sodium amalgam (see below). The salt also changes into the azine of phenylglyoxylic acid, $N_2({:}CPh \cdot CO_2H)_2$ (Bouveault, A., 1898, i, 585), when mixed with hydrochloric acid, and the same product may be obtained by warming phenylglyoxylic acid with hydrazine sulphate solution. The azine yields *hydrazophenylacetic acid*, $N_2H_2(CHPh \cdot CO_2H)_2$, m. p. 160—161°, on reduction with sodium amalgam, and this gives an *ethyl* ester, slender needles, m. p. 88—89°.

II. ACTION OF HYDRAZINE HYDRATE ON BROMOACETIC, α-BROMOPROPIONIC, α-BROMOISOVALERIC, BROMOMALONIC, AND BROMOPHENYLACETIC ACIDS, pp. 280—300 [with MORESHWAR PRABHAKAR].—The hydrochlorides of ethyl hydrazinoacetate (Traube and Hoffa, A., 1898, i. 235) and ethyl α-hydrazinopropionate (above) may be prepared by boiling together alcoholic solutions of hydrazine hydrate and the corresponding bromo-acids, and then saturating the mixtures with hydrogen chloride. α-*Hydrazino*isovaleric *acid*,

$$N_2H_3 \cdot CHPr^{\beta} \cdot CO_2H,$$

separates in sparingly soluble leaflets, m. p. 230—235° (decomp.),

when hydrazine hydrate and α-bromo*iso*valeric acid are boiled together in alcohol; it forms a *benzylidene* compound, m. p. 121°, and a *diacetyl* derivative, m. p. 205°. Bromomalonic acid gives the *dihydrazine* salt of *hydrazinodimalonic acid*,

$$NH_2\cdot N[CH(CO_2H)_2,N_2H_4]_2,$$

in long, pale yellow needles, m. p. 209° (decomp.). Bromophenylacetic acid (from mandelic acid and hydrobromic acid) yields *hydrazinophenylacetic acid*, $N_2H_3\cdot CHPh\cdot CO_2H$ (above), in white leaflets, m. p. 189—190° (decomp.). This forms a *benzylidene compound, m. p. 150°, a salicylidene compound, m. p. 153—154°*, and a *dibenzoyl* derivative, m. p. 169·5—170°. It is oxidised by ferric chloride to benzaldazine and hydrazine chloride, and is converted into chloro- and bromo-phenylacetic acids by means of the halogens, and into mandelic acid by means of nitrous acid. The *ethyl* ester is an insoluble, yellow oil, which forms a *hydrochloride*, m. p. 138° (decomp.), a *hydrobromide*, m. p. 142·5°, and a *salicylidene* compound, slender, pale yellow needles, m. p. 107°, and reacts with chlorine to give ethyl chlorophenylacetate. The *methyl* ester also yields a *hydrochloride*, m. p. 148—148·5°. The salts of the esters react with potassium cyanate to give esters of *carbamylhydrazinophenylacetic acid*, $NH_2\cdot CO\cdot N(NH_2)\cdot CHPh\cdot CO_2R$. The *ethyl* ester has m. p. 102·5—103°, and forms a *hydrochloride*, m. p. 153°, and *salicylidene* compound, m. p. 149·5°. The *methyl* ester has m. p. 141°. The hydrochloride of the ethyl ester also reacts with sodium nitrite to form *ethyl nitrosohydrazinophenylacetate*, $NH_2\cdot N(NO)\cdot CHPh\cdot CO_2Et$, in silky needles, m. p. 59°, which gives the violet coloration with ferric chloride typical of nitrosohydrazines. This ester reacts with a further quantity of nitrous acid to give ethyl phenyldiazoacetate and then ethyl mandelate, decomposes at 110° into nitrous oxide and ethyl phenylglycine, and changes into ethyl triazophenylacetate,

$$N_3\cdot CHPh\cdot CO_2Et$$

(Forster and Müller, T., 1910, **97**, 138), when distilled with 10% sulphuric acid.

III. ACTION OF HYDRAZINE HYDRATE ON α- AND β-BROMO-β-PHENYLPROPIONIC ACID, pp. 301—327 [with HERBERT BERGER].—α-Bromo-β-phenylpropionic acid is obtained as follows: ethyl benzylmalonate (Leuchs, A., 1911, i, 602) is hydrolysed by shaking it with an excess of potassium hydroxide (5 mols.), the free acid is then brominated in ethereal solution, and the bromobenzylmalonic acid is heated at 125—130°. The acid is converted into α-hydrazino-β-phenylpropionic acid, $NH_2\cdot NH\cdot CH(CH_2Ph)\cdot CO_2H$, by means of alcoholic hydrazine hydrate, and the product agrees with Traube and Longinescu's description (*loc. cit.*). It forms a *hydrochloride*, benzylidene and salicylidene compounds (*ibid.*), a *diacetyl* derivative, transparent tablets, m. p. 190—191°, a *dibenzoyl* derivative, rhombic needles, m. p. 190—192°, and it reacts with sodium nitrite and dilute sulphuric acid to give α-hydroxy-β-phenylpropionic acid (Fischer and Zemplén, A., 1910, i, 100). It also reacts with alcoholic hydrogen haloids to give the

hydrochloride (leaflets, m. p. 125°) and *hydrobromide* (snow-white leaflets, m. p. 123—125°) of the *ethyl* ester, this being a yellow oil, which changes when kept or heated (125°/14 mm.) into ethyl β-phenylpropionate. The hydrobromide yields *ethyl α-bromo-β-phenylpropionate*, b. p. 169°/14—15 mm., when treated with bromine in hydrobromic acid solution, whilst the hydrochloride may be converted into the *p-nitrobenzylidene* compound,

$$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot NH \cdot CH(CH_2Ph) \cdot CO_2Et,$$

yellow rhombohedra, m. p. 87°, *ethyl α-semicarbazido-β-phenylpropionate*, $NH_2 \cdot CO \cdot NH \cdot NH \cdot CH(CH_2Ph) \cdot CO_2Et$, needles, m. p. 147° (by means of potassium cyanate), and *ethyl α-nitrosohydrazino-β-phenylpropionate*, $NH_2 \cdot N(NO) \cdot CH(CH_2Ph) \cdot CO_2Et$, pale yellow, silky needles, m. p. 61° (by means of a concentrated solution of sodium nitrite). The nitroso-ester is decomposed by heat (115—120°) into nitrous oxide and the ethyl ester of phenylalanine, whilst on warming with dilute sulphuric acid it yields the *ethyl* ester (b. p. 154°/14 mm.) of *α-azido-β-phenylpropionic acid*, $CH_2Ph \cdot CHN_3 \cdot CO_2H$, this crystallising in large tablets, m. p. 24—27°, and forming an *ammonium* and a *silver* salt.

β-Bromo-β-phenylpropionic acid (from cinnamic acid and hydrogen bromide) reacts in quite another way with hydrazine hydrate. The product has the expected formula, but it is insoluble in alkalis and may be hydrolysed by hydrochloric acid. It is, in fact, *β-hydroxy-β-phenylpropionhydrazide*,

$$OH \cdot CHPh \cdot CH_2 \cdot CO \cdot NH \cdot NH_2,$$

which crystallises in slender needles, m. p. 158°, and it is accompanied by some styrene and cinnamic acid. The hydrazide may also be prepared by the action of hydrazine hydrate on ethyl β-hydroxy-β-phenylpropionate (Findlay and Hickmans, T., 1909, **95**, 1009). It forms a *benzylidene* compound, glistening leaflets, m. p. 179°, and reacts with nitrous acid to give the *azide*,

$$OH \cdot CHPh \cdot CH_2 \cdot CO \cdot N_3,$$

a pale yellow oil, which changes into *β-hydroxy-β-phenylpropionanilide*, m. p. 160°, when mixed with aniline.

It is mentioned that an alcoholic solution of hydrogen bromide can be obtained most readily by passing a current of dry hydrogen through warm bromine, then over platinised asbestos heated by a small flame, next through a tube containing red phosphorus, and finally into the alcohol. J. C. W.

The Methylation of Proteins. J. HERZIG and KARL LANDSTEINER (*Monatsh.*, 1918, **39**, 269—284. Compare A., 1914, i, 753).—In the earlier investigation, it was shown that for various proteins the action of diazomethane gives products containing a fairly uniform percentage of methyl radicle, as indicated by the figures 3·68—4·86% of methoxyl group and 3·72—5·34% of methyl attached to nitrogen; silk fibroin alone was exceptional, the product from this containing 2·79% of methoxyl and 4·93% of iminomethyl, even after repeated methylation. Wool, after being submitted repeatedly to the action of diazomethane, contains 5·89%

of methoxyl and 6·28% of imino-methyl. In a similar examination of the alcohol-soluble proteins from grain, it was found that the zein of maize is rather resistant to diazomethane, giving after several treatments a product containing 4·17% of methoxyl and only 2·9% of imino-methyl; gliadin from wheat is more reactive, and gives a product containing 7·06% of methoxyl and 2·56% of imino-methyl. Non-coagulated serum-albumin from the horse gives results similar to those obtained with the coagulated product (*loc. cit.*).

[With F. ZIPPERER and M. QUITTNER.]—A similar examination was made of the effect on proteins of a ten-hour treatment with a boiling 1% solution of hydrogen chloride in methyl alcohol; the products gave the following analytical results: silk fibroin, 1·4% of methoxyl, imino-methyl proportion almost identical with that of the original substance; wool, 3·80% of methoxyl, 1·49% of imino-methyl. With zein, and particularly with gliadin, the hydrogen chloride causes considerable hydrolysis, a similar result being also obtained in the treatment of Witte's peptone. The product from zein contains 5·47—6·18% of methoxyl, but the imino-methyl content is almost unaltered. With gliadin, a large proportion passes into solution, the undissolved residue, as well as the portion of the dissolved material precipitable by ether, containing approximately 7% of methoxyl; it is probable that the extent of the hydrolytic effect of the methyl-alcoholic acid is greater than these figures indicate, because the resulting glutamic acid is remarkably resistant to esterification by this reagent. It is also probable that to some extent esterification products formed in the earlier stages of the treatment undergo subsequent hydrolysis by the action of water resulting from the interaction of the hydrogen chloride and methyl alcohol. The product of the reaction between zein or gliadin and methyl-alcoholic hydrogen chloride on treatment with diazomethane undergoes a marked increase in methoxyl content, which, however, is probably due in part to the presence of phenolic groups.

D. F. T.

Legumin in Peas. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 85—104).—The legumin prepared from peas by extraction with salt solution and subsequent removal of the salt by dialysis (Osborne, A., 1896, i, 715) is soluble in dilute salt solutions, and thus differs from the insoluble legumin obtained from peas by extraction with water or dilute alkali, followed by precipitation with dilute acetic acid (Ritthausen, *J. pr. Chem.*, 1868, **103**). The author proposes to designate the former as *a*-legumin and the latter as *b*-legumin. *b*-Legumin appears to be an acid meta-protein. *a*-Legumin also forms a compound with acid, which, however, is not *b*-legumin, because the latter swells in water, giving a viscid, non-filterable solution, whereas the acid compound of *a*-legumin does not swell in water, but gives a limpid, milky emulsion which filters readily, yielding an opalescent filtrate. Other slight differences in the properties of *a*- and *b*-legumins are

described, which indicate that *b*-legumin is not formed from *a*-legumin by the action of acid, alkali, or water, but is a distinct protein. H. W. B.

Hæmoglobin, Bilirubin, and Urobilinogen. W. C. DE GRAAFF (*Chem. Weekblad*, 1918, **15**, 1032—1045, 1059—1071).—A summary of the literature of the subject. A. J. W.

Influence of Electrolytes on the Osmotic Pressure of Gelatin Solutions. JACQUES LOEB (*J. Biol. Chem.*, 1918, **35**, 497—508. Compare this vol., i, 413).—The osmotic pressures of solutions of gelatin which has been treated with acids, bases, and salts by the author's method (*loc. cit.*) are affected by the preliminary treatment which the gelatin has received in exactly the same way as the other properties so far examined, namely, swelling, viscosity, and resistance to precipitation by alcohol. The measurements were carried out by Lillie's method (A., 1907, ii, 847), and the results demonstrate that gelatin treated with neutral salts and bases with univalent cation and acids with univalent anion has a greater osmotic pressure when dissolved in water than a solution of untreated gelatin, whilst salts and bases with bivalent cation and acids with bivalent anion do not produce any effect on the gelatin. H. W. B.

Action of Chymosin and Pepsin. V. Action of the Enzymes on Legumin from Peas. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 105—147. Compare this vol., i, 459).—Chymosin acts on other proteins besides caseinogen, forming albumoses. Acid- and alkali-legumin are hydrolysed by chymosin in neutral solutions or in the presence of so little acid that any pepsin present would exert no, or but very little, hydrolytic action. The results are considered by the author to support the theory that assigns a separate identity to chymosin and pepsin. H. W. B.

New Salts of 1 : 1-Dimethylarsepedine. ENRIQUE V. ZAPPI and JUAN L. LANDABURU (*Bull. Soc. chim.*, 1918, [iv], **23**, 324—326. Compare A., 1916, i, 575, 683).—The salts were prepared by neutralising a solution of 1 : 1-dimethylarsepedine hydroxide (*loc. cit.*, i, 575) in the presence of phenolphthalein with the requisite acid, the solution being evaporated to dryness over sulphuric acid and sodium hydroxide.

1 : 1-*Dimethylarsepedine methochloride*, $CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>AsMe_2Cl$, has m. p. 237° (decomp.); the *methobromide*, m. p. 277—280° (decomp.).

1 : 1-*Dimethylarsepedine sulphate* has m. p. 232° (decomp.); the *nitrate*, m. p. 260° (decomp.); the *hydrogen carbonate*, $C_8H_{16}As,HCO_3$, m. p. 156—157° (decomp.). W. G.

Physiological Chemistry.

The Haldane-Henderson Method for Estimating the [T]ension of Alveolar Carbon Dioxide and the Influence of [O]xygen on the Stimulability of the Respiratory Centres. [M]OTOI YAMADA (*Biochem. Zeitsch.*, 1918, **89**, 27—47).—A new [v]alve is described and figured for use with Henderson's modification [o]f Haldane's method for estimating alveolar carbon dioxide. It [w]as found that when the amount of carbon dioxide inhaled was [g]reater than normal, the alveolar ventilation was better when the [g]as was mixed with pure oxygen than when mixed with air. Hence [o]xygen has a favourable influence on the breathing centre. No [i]nfluence could be found to be exerted on the respiratory centre by [t]he inhalation of pure oxygen. S. B. S.

The Influence of Atropine on Respiratory Metabolism [a]nd the Blood Gases. GEORG KELEMAN (*Biochem. Zeitsch.*, [1]918, **89**, 338—349).—There is a marked diminution of the [r]espiratory metabolism of dogs after intravenous injection of [a]tropine, which effect can be antagonised by the simultaneous [i]njection of pilocarpine. The increased gaseous metabolism pro[d]uced by pilocarpine can be diminished by atropine, and the [d]iminished gaseous metabolism produced by the latter alkaloid can [b]e increased by the subsequent injection of the former. The con[t]ent of the blood in carbon dioxide is diminished by injection of [a]tropine. The diminished output of carbon dioxide produced by [i]njection of atropine, already mentioned, is due, therefore, not to [a] diminished secretion of this gas by the lungs, but to a general [d]iminution of its production. S. B. S.

The Action of Pilocarpine on Respiratory Metabolism [a]nd the Gas Content of the Blood. G. KELEMAN (*Biochem. [Z]eitsch.*, 1918, **89**, 135—155).—The increased secretory activity of [t]he salivary glands produced by pilocarpine is accompanied by an [i]ncreased metabolism of energy (about 10%). There is also pro[d]uced at the same time an increased carbon dioxide content in the [b]lood, both venous and arterial. There is no evidence, however, [o]f an increased "secretion" of carbon dioxide by the blood.

S. B. S.

The Agglutination of Red Blood Corpuscles and the Hof[m]eister Series. W. RADSMA (*Biochem. Zeitsch.*, 1918, **89**, [2]11—219).—Blood corpuscles, suspended in a large amount of [is]otonic solution of dextrose, readily agglutinate on addition of a [sm]all amount of a salt; 0·04% of sodium chloride is sufficient to bring [ab]out this phenomenon. The anions, in their activity as regards [th]is agglutinative effect, follow the order of the Hofmeister series,

and this indicates that some hydrophil colloid plays a part in maintaining the stability of a suspension of the corpuscles. S. B. S.

The Action of Chlorates on the Blood of Man and certain Animals. EGBERT CAESAR (*Biochem. Zeitsch.*, 1918, **89**, 1—26).—Details are given as to the concentrations in which potassium chlorate exerts an injurious action on the blood, giving rise to the formation of methæmoglobin. The general conclusion is drawn that potassium chlorate can act toxically when taken *per os*, and that it should not be used indiscriminately in tooth-powders and analogous preparations. The astringent action of aluminium chlorate is due to the aluminium ion. A detailed criticism is given of a commercial preparation of chlorates known as Mallebrein's.
S. B. S.

Clinical Value of Freezing-point Determinations. FRITZ EIGENBERGER (*Zeitsch. physiol. Chem.*, 1918, **102**, 166—175).—The addition of urea, dextrose, or sodium chloride to a colloidal solution of gelatin, starch, or blood-serum produces scarcely any lowering of the freezing point, measured by Beckmann's method. When an acid or an alkali is added, a considerable depression may be observed, but it does not equal the calculated value. The author draws the conclusion that the determination of the freezing point of a pathological serum is not likely to furnish any valuable clinical information. H. W. B.

The Influence of Oxygen on Metabolism. I. Experiments on Meal-worms. TORBJÖRN GAARDER (*Biochem. Zeitsch.*, 1918, **89**, 48—93).—The metabolism of the *Tenebrio* chrysalis is independent of the oxygen tension of the atmosphere as long as the oxygen tension of the tissues is positive. As the oxygen tension of the atmosphere sinks, the gradient between the oxygen tension of the tissues and the atmosphere remains constant, until the former tension becomes zero. With further diminution of the tension of the oxygen of the atmosphere beyond this point, the gradient of oxygen tension between the tissue and atmosphere sinks, and the oxygen consumption of the chrysalis diminishes. Numerous numerical data are given in support of these statements, and the experiments were carried out by means of a modified micro-respirator of Krogh. If the chrysalis is allowed to remain in an atmosphere so poor in oxygen that the metabolism is sub-normal, certain anaerobic processes take place. On removing the animal to an atmosphere of normal oxygen content, the metabolism remains for some time sub-normal; it then increases and becomes greater than normal, and this is apparently due to the destruction of products formed during the anaerobic conditions. S. B. S.

The Influence of Oxygen Tension on Metabolism. II. Experiments with Carp. TORBJÖRN GAARDER (*Biochem. Zeitsch.*, 1918, **89**, 94—125).—An apparatus is figured and described for

passing water with known oxygen content through the gills of fish and estimating the consumption. It is found that there is a very slow increase in oxygen consumption with increasing tension of the oxygen dissolved in water. The increase is so small that the conclusion is drawn that the changes in oxygen tension in water which take place normally are without any appreciable effect on the metabolism. There is a linear relationship between oxygen consumption and the oxygen tension of the water passing the gills, that is, the oxygen consumption is in accordance with laws governing the absorption of gases by a liquid, and the increase of the consumption can be explained by assuming that the oxygen dissolved physically in the blood is utilised. S. B. S.

Metabolism of Glycine given Intravenously at Constant Rates. JULIAN H. LEWIS (*J. Biol. Chem.*, 1918, **35**, 567—576).—Glycine can be injected intravenously into a dog at the rate of 0·2 gram per kilo. of body weight per hour without causing the appearance of the amino-acid in the urine. The nitrogen is subsequently excreted at a slower rate in the form of urea.

H. W. B.

Significance of Glycollic Acid, Glyoxal, Glycollaldehyde, and Aminoacetaldehyde in Intermediary Metabolism. ISIDOR GREENWALD (*J. Biol. Chem.*, 1918, **35**, 461—472).—The subcutaneous injection of glycollaldehyde and aminoacetaldehyde into phloridzinised dogs is followed in each case by an increased elimination of dextrose; similar injections of glyoxal or glycollic acid do not intensify the glycosuria. These results favour the view that glycine and dextrose are interchangeable in the organism in the following manner: glycine $\rightleftharpoons$ aminoacetaldehyde $\rightleftharpoons$ glycollaldehyde $\rightleftharpoons$ dextrose. H. W. B.

Nuclein Metabolism. V. Destruction of the Purine Ring by Bacteria in the Human Intestine. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1918, **102**, 148—159. Compare this vol., i, 47).—After twenty days' incubation of adenosine, guanosine, or inosine with a culture of bacteria from the human intestine, from 60 to 100% of the nitrogen in the nucleoside is found to have been converted into ammonia. These results are in harmony with and explain the observation that the purines in ingested nucleic acid are not quantitatively excreted in the form of uric acid, but to a certain extent undergo degradation in the body and are eliminated as urea (doubtless through the intermediate formation of ammonia by the action of the intestinal bacteria). H. W. B.

Fat soluble Vitamine. I. H. STEENBOCK, P. W. BOUTWELL, and HAZEL E. KENT (*J. Biol. Chem.*, 1918, **35**, 517—526).—Experiments on rats are described, the results of which indicate

that the fat-soluble vitamine in butter-fat is destroyed by heating the butter-fat at 100° for four hours. H. W. B.

The Changes of Condition in Tissue Colloids Associated with the Healing of Wounds. W. von Gaza (*Kolloid Zeitsch.*, 1918, **23**, [i], 1—11).—A discussion of the healing of wounds in the light of modern conceptions of colloid chemistry. E. H. R.

Indicators in Animal Tissues. W. J. Crozier (*J. Biol. Chem.*, 1918, **35**, 455—460. Compare A., 1916, ii, 337).—The hydrozoan *Velella velella*, L., contains a blue pigment which gives an orange extract with 70% alcohol. It is made bright orange by alkalis and decolorised by acids.

Two sponges, "A" and "B," members of the *Aplysinidæ*, have yielded coloured aqueous extracts; one is turned bright yellow by acids and blue to purple by alkalis; the other is a crimson-coloured extract, turned violet by acids and yellow by alkalis.

The anterior portion of the œsophagus of the large holothurian *Stichopus moebii*, Semp., contains a reddish-purple echinochrome which is not readily extracted from the tissue. Alkalis intensify the colour; acids change it to bright orange.

By comparing the colour of the natural tissue with the extracted pigment, it is possible to draw some conclusions regarding the degree of acidity or alkalinity of the tissue cells. The tissues of marine animals are in general more acid than the surrounding sea-water, the hydrogen-ion concentration varying between $p_H = 6 \cdot 0$ and $p_H = 7 \cdot 6$, and increasing when death ensues to $p_H = 5$ to 6. Higher alkalinity in the protoplasmic juices of young, rapidly growing individuals has never been observed in these pigmented animals, the normal reaction of the cells concerned being acid rather than alkaline. H. W. B.

The Phosphorus in Organic Combination in Human Urine. Observation in Acute Yellow Atrophy of the Liver. Joh. Feigl (*Biochem. Zeitsch.*, 1918, **89**, 126—134).—Chiefly a review of the literature and of methods. S. B. S.

The Biochemical Behaviour of Aminomethyl Hydrogen Sulphite. E. Salkowski (*Biochem. Zeitsch.*, 1918, **89**, 178—198).—Aminomethyl hydrogen sulphite, $NH_2 \cdot CH_2 \cdot O \cdot SO_2H$ (Reinking, Dehnel, and Labhardt, A., 1905, i, 261), yields formaldehyde in the distillate when an aqueous solution is distilled, and also, but very slowly, when it is kept in water at ordinary temperatures. Experiments with urine and meat indicate that it is of little value as an antiseptic. No formaldehyde could be detected in the urine after administration of the acid to a rabbit. When administered to a dog, part appears, from the increase of the neutral sulphur in the urine, to be excreted unchanged. Indican disappears from the urine during administration, and this fact seems to indicate that aminomethyl hydrogen sulphite acts as an intestinal antiseptic. S. B. S.

The Photolytic and Photodynamic Action of an α-Furo-β-diazole. P. R. Kögel (*Biochem. Zeitsch.*, 1918, **89**, 204—210).—The substance employed was β-naphthoxadiazole-4-sulphonic acid, which undergoes change on exposure to light. The photodynamic effects were demonstrated on the protozoon *Colpidium colpoda*. S. B. S.

Physiological Action of Hydroatophan. Julius Pohl (*Zeitsch. J. exper. Path. Ther.*, 1917, **19**, 198—204; from *Chem. Zentr.*, 1918, i, 929).—Experiments on the frog show that the action of the atophan molecule on the heart is completely altered by hydrogenation and is replaced by a spinal and peripheral excitation. Toxicity towards warm-blooded animals is characterised by increased excitability of the spinal reflexes. H. W.

The Influence of Temperature on the Strength of Action and Surface Activity of Narcotics. Rudolf Unger (*Biochem. Zeitsch.*, 1918, **89**, 238—278).—The influence of changes of temperature on narcotic activity of various substances, such as chloral hydrate, salicylamide, benzamide, monoacetin, and ethyl alcohol, was investigated, the subjects of experiment used being tadpoles, the fish *Leuciscus*, and the sciatic nerve of frogs. In some cases, increase of temperature increased, and in others it diminished narcotic activity. These changes could not always, however, be correlated with changes in the distribution of the narcotic between oil and water, as would follow from the Overton-Meyer theory, or with the change in surface tensions of the solutions. Account has to be taken in investigations of this character of the effect of temperature changes on the general metabolic activity. S. B. S.

Relation between the Chemical Structure of the Opium Alkaloids and their Physiological Action on Smooth Muscle with a Pharmacological and Therapeutic Study of some Benzyl Esters. II. Pharmacological and Therapeutic Study of some Benzyl Esters. David I. Macht (*J. Pharm. Expt. Ther.*, 1918, **11**, 419—446. Compare this vol., i, 418).—Benzyl acetate and benzoate produce the same effects on smooth muscle as papaverine, but are comparatively non-toxic; they may therefore be employed clinically to alleviate conditions of excessive peristalsis or spasms of viscera containing smooth muscle fibres. Beneficial effects have been observed to follow the administration of one or other of these esters in cases of chronic diarrhœa, dysentery, asthma, etc. H. W. B.

Relations between the Constitution and the [Physiological] Activity of *ac*-Tetrahydro-β-naphthylamine and its Derivatives. Ernst Waser (*Schweiz. Chem.-Zeit.*, 1917, **1**, 12—15; from *Chem. Zentr.*, 1918, i, 830).—Derivatives of *ac*-tetrahydro-β-naphthylamine have been examined with the object of

finding one having a quicker and more powerful fever-producing action than the base itself. Experiments undertaken to bring the base into an active, fever-producing form show that in this case Gros's theory, according to which the anæsthetic potential of a salt is proportional to its degree of hydrolytic dissociation, does not hold. There is no appreciable difference in the physiological activity of *ac*-tetrahydro-β-naphthylamine and its optically active modifications. The entrance of acyl groups produced a diminution of the activity instead of the expected increase. Whilst the acetyl derivative is much more poisonous to frogs, the converse is the case with warm-blooded creatures (dogs), in which the base itself produces strong dilatation of the pupil and increase of the temperature and the blood-pressure, whilst the acetyl derivative produces contraction of the pupil and a lowering of the temperature and the blood-pressure. A similar behaviour is also shown by the ·CHO, ·COPh, ·CO_2Et, ·CO·NHPh, ·CS·NHPh, and ·CS·NHEt derivatives. Of the alkyl derivatives, the monomethylated base serves the author's purpose, since in small doses it produces a relatively high feverishness in the shortest time. The ethyl derivative acts ike *ac*-tetrahydro-β-naphthylamine itself. It has been found that *ac*-tetrahydro-β-naphthylamine produces complete immunity against any further injection of itself or of the methyl and ethyl derivatives, that the methyl derivative produces immunity against itself and the ethyl derivative, and that the latter only produces mmunity against itself. *N*-Acyl-*N*-alkyl derivatives produce effects which are a combination of those of the mono-substituted lerivatives. Thus injection into dogs of *N*-acetyl(or formyl)-*N*-nethyl-*ac*-tetrahydro-β-naphthylamine produces on the one hand lilatation of the pupil (effect of the methyl derivative) and on the other a lowering of the temperature (effect of the acyl derivative). Experiment shows that a portion of the substance is hydrolysed in the organs (of warm-blooded animals); the resulting methyl derivative or *ac*-tetrahydro-β-naphthylamine itself suffices not only to uppress the myotic action of the acyl group, but even to reverse t, but is insufficient to influence the temperature effect. All the esults are tabulated. C. S.

Chemistry of Vegetable Physiology and Agriculture.

Problems of Bacteria Adsorption. H. Bechhold (*Kolloid Zeitsch.*, 1918, **23**, 35—43).—In the course of a research on the dsorption of bacteria by different materials, experiments were nade on the adsorption of certain dyes by the same adsorbents. The basic dye, methylene-blue, was strongly adsorbed by a variety

of substances, such as animal and vegetable charcoal, fuller's earth, bolus, clay, permutite, and silicic acid, whilst trypan-blue, which is acidic, was adsorbed only by charcoal and ferric hydroxide. There is a strong resemblance between the relative adsorptive powers of the above materials for bacteria (*Staphylococcus* and *Bacterium coli*) and for methylene-blue, although ferric hydroxide adsorbs the bacteria and not the colour. Charcoal and fuller's earth surpass any other adsorbent materials, although the mean diameter of their particles may be greater than that of the less adsorbent substances. E. H. R.

The Catalase of Bacteria. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **89**, 350—354).—The paper describes attempts to prepare a pure catalase. *Bacillus proteus* was grown on the medium already employed by the author, which contains, besides the inorganic salts, sodium aspartate and sodium lactate. From such cultures, an active catalase could be obtained by precipitation with ammoninm sulphate, magnesium sulphate, and sodium chloride. The precipitate obtained was dissolved in water. A catalase could also be precipitated by mercuric chloride; in this case, an active preparation was obtained by redissolving the precipitate in potassium cyanide solution. S. B. S.

Chemical Composition and Formation of Enzymes. XV. Further Experiments with Bacterium Acidi lactis (Streptococcus lactis). HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1918, **102**, 176—184. Compare this vol., i, 55, and Euler and Griese, A., 1917, i, 679).—The lactic acid fermentation of lactose by *Streptococcus lactis* is not accelerated, but rather inhibited by sodium dihydrogen phosphate, and in these new experiments an evolution of carbon dioxide has not been observed. The difference between these results and those formerly described (*loc. cit.*), may be due to the employment of a different species of bacterium or to a contamination in the earlier experiments of the bacteria with yeast cells or other micro-organisms. The presence of sodium lactate appears to exert an inhibiting action on the formation of lactic acid by the bacteria. H. W. B.

The Arrest of Alcoholic Fermentation in the Aldehyde Stage. An Experimental Confirmation of the Acetaldehyde Pyruvic Acid Theory. CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1918, **89**, 365—414).—Neuberg has shown that yeast contains a ferment which decomposes pyruvic acid into acetaldehyde and carbon dioxide; furthermore, acetaldehyde is readily reduced during yeast formentations to ethyl alcohol. It seemed therefore probable that acetaldehyde is an intermediate product in alcoholic fermentation. The authors now show that considerable amounts of acetaldehyde can be obtained in the ordinary yeast fermentations of sugars, and can be isolated if the fermentation is

carried out in the presence of sodium sulphite. The equations representing the reactions may be represented as follows:

(*a*) $C_6H_{12}O_6 + Na_2SO_3 + H_2O = C_6H_{12}O_5(OH)\cdot O\cdot SO_2Na + NaOH$.
(*b*) $\frac{1}{2}C_6H_{12}O_5(OH)\cdot O\cdot SO_2Na = H_2 + CH_3\cdot C(OH)(CO_2H)\cdot O\cdot SO_2Na$.
(*c*) $CH_3\cdot C(OH)(CO_2H)\cdot O\cdot SO_2Na_2 = CH_3\cdot CH(OH)\cdot O\cdot SO_2Na + CO_2$.
(*d*) $NaOH + CO_2 = NaHCO_3$.

As one-half of the molecule should yield aldehyde, which acts as acceptor for the hydrogen evolved, it should not be expected that one molecule of sugar should yield more than one molecule of carbon dioxide and one molecule of aldehyde.

$$C_6H_{12}O_6 = CH_3\cdot CHO + CO_2 + \left[\left\{\frac{C_6H_{12}O_6}{2}\right\}H_2\right].$$

An amount of aldehyde equivalent to 73·45% obtainable on this theory has been obtained.

Full details are given of the methods employed for the quantitative estimation of the aldehyde and alcohol formed during fermentation. S. B. S.

Willstätter's Researches on the Assimilation of Carbon Dioxide. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 1138—1146). —A review of the recent work of Willstätter on this subject. A. J. W.

The Physiological Significance of Potassium in Plants. TH. WEEVERS (*Biochem. Zeitsch.*, 1918, **89**, 281—282).—A final reply to Stoklasa (A., 1917, i, 682). S. B. S.

Active Principles of the Horse Chestnut. GEORGES MASSON (*Bull. Sci. Pharmacol.*, 1918, **25**, 65—72; from *Chem. Zentr.*, 1918, ii, 40—41).—Separate examination of the seed capsules and cotyledons has led the author to revise his previous conclusions (*Diss.*, Paris, 1910).

The seed capsules yield, after extraction with alcohol, an almost fat-free, bright red residue which gives red needles when crystallised from water; the compound shows tannin reactions, and is transformed by warm sulphuric acid into gallic acid and a red substance.

From the fat-free cotyledons, two acids are obtained: (1) *Aesculic acid*, fine needles, m. p. 214—215°, which are insoluble in water. The salts are yellow and amorphous. The *barium*, *calcium*, *magnesium*, and *lead* salts were investigated. Protracted boiling of an alcoholic solution of the acid which has been treated with 5% sulphuric acid slowly causes hydrolysis with formation of a reducing sugar. (2) *Aesculinic acid*, golden-yellow, apparently crystalline needles, m. p. 230—231°, lævorotatory, soluble in water. The *alkali* and *barium* salts are yellow and soluble in water; their solutions have emulsifying properties. The *lead* salt is insoluble in water. The acid is hydrolysed, even by dilute acids, to a reducing sugar and a new *acid*. The reducing sugars produced from æsculic and æsculinic acids consist of a mixture of mannose and dextrose.

It appears, therefore, that the seed capsules contain a tannin yielding gallic acid. Two glucosidic saponins are present in the cotyledons, of which the insoluble æsculic acid is emulsified by the aqueous solutions of the æsculinic acid; the mixture of acids constitutes the active principle of the seeds, previously termed argyrescin or aphrodescin. If the whole fruit is examined, the presence of the gallic acid of the capsules causes the formation of tannin compounds having properties differing from those of the glucosides. H. W.

[**The Pigment of Myrtle Berries and its Use as an Indicator.**] C. MARINI (*Annali Chim. Appl.*, 1918, **10**, 32—36).—The pigment of myrtle berries (*Vaccinius myrtillus*, L.) appears to be identical with œnocyanin, the red colouring matter of wine, to which Glenard (*Ann. Chim. Phys.*, 1858, [iii], **54**, 369) assigned the formula $C_{20}H_9O_2$, the œnolic acid in which combines with bases to form salts. The pigment of myrtle berries may be extracted with 50% alcohol and precipitated with basic lead acetate. By digesting the washed and dried precipitate, first with ether saturated with hydrogen chloride, then with ether, and finally digesting the insoluble portion with alcohol, and treating the alcoholic extract with ether, a carmine-red pigment is precipitated. This consists of two components, one of which is insoluble in hot water, whilst the other, $C_{20}H_{14}O_{12}$, which predominates, is soluble in acidified water, and when boiled with acids is converted into the first component, with the elimination of dextrose. It thus appears to be a glucosidal compound, and is probably a glucotannoid. The pigment extracted from the berries with 90% alcohol acts as a weak acid and forms green salts with alkalis. Test papers, which are more sensitive than turmeric paper, may be prepared from it for use as indicators of acidity or alkalinity. C. A. M.

Pollen and Pollen Disease. I. Chemical Composition of Ragweed Pollen. JESSIE HORTON KOESSLER (*J. Biol. Chem.*, 1918, **35**, 415—424).—The pollen grains of ragweed (*Ambrosia artemisifolia* and *A. trifida*), which produce hay fever in certain susceptible persons, contain about 10·5% of water, 10·6% of mineral matter, and 78·9% of organic substances, including 7% of sugars, 10% of lipoids, consisting of fats and phytosterol, and 37% of proteins, crude fibre, etc. The dry pollen contains 4·7% of nitrogen. H. W. B.

Absorptive Power of Zeolitic Bases of Soil. K. K. GEDROITZ (Reprint, pp. 1—55).—Black soil has been treated with $0.2N$-, N-, and $4N$-solutions of a number of chlorides, both separately and together, this treatment being repeated until the bases were completely extracted; the results obtained are as follows.

All the zeolitic bases of a soil may be displaced by a certain cation. The bulk of these bases consists of lime (almost 75%), the remainder being magnesia (20%), soda, potash, and possibly manganese oxide. The extraction of soils with hydrochloric acid (about

10%) for the estimation of the zeolitic part gives certain results only for the zeolitic lime, the proportions of the other bases found being too high. Iron and aluminium do not occur in soils—even the red soils of Algeria—as zeolitic bases in detectable proportion.

All the zeolitic bases of a natural soil may be displaced completely by any base either ordinarily present or not in the soil. Except with soils not saturated by bases, the quantity of base absorbed is equivalent to the quantity of bases displaced from the zeolitic part of the soil.

Soil saturated by any base or bases contains this base or bases in the zeolitic part in such quantities as, expressed in equivalents, are independent of the nature of the bases.

The energy of absorption varies with different cations, and is greatest with tervalent and less with bivalent cations; calcium is absorbed more energetically than magnesium. Univalent cations are still more feebly absorbed, sodium more so than potassium.

The relation of the qualitative and quantitative composition of the zeolitic bases of soils to the life of the soil and plant and various other questions are discussed. T. H. P.

Saline Soils and their Improvement. K. K. Gedroitz (Reprint, pp. 1—16).—The author describes the treatment necessary for the improvement of soils (1) containing an excess of neutral salts, such as the so-called white alkali land, and (2) containing soda, such as the black alkali land. T. H. P.

The Inversion of Cane-sugar by Soils and Allied Substances and the Nature of Soil Acidity. F. E. Rice *and* S. Osugi (*Soil Science*, 1918, **5**, 333—358).—It is shown that soils of many kinds can cause the inversion of sucrose, this power being a property of the mineral portion as well as of the organic matter of the soil. This effect is due to acid, which may be present as a slight amount soluble in the sugar solution or in one of three insoluble forms: (*a*) acids ordinarily easily soluble, but in the soil strongly adsorbed on the soil particle surfaces; (*b*) an insoluble acid, such as silicic acid; (*c*) acid liberated from a neutral salt present in the soil solution by its breaking down, owing to the base being more strongly adsorbed than the acid, this being thus left free to cause inversion of the sugar. Many soils showed inverting action on sucrose in a solution which remained neutral or, in some cases, became alkaline after contact with the soil. Silicate minerals may be given inverting power by submitting aqueous suspensions to a direct current, and soil acidity is increased by a similar treatment of soils. Contrary to previous conclusions, hydrated oxides of lead, copper, bismuth, aluminium, iron, and zinc were not found to have any inverting power.

The authors consider that the measurement of the power of a soil to catalyse the inversion of cane-sugar is probably the only method by which the acidity bound up with the solid phase of the soil can be measured. W. G.

Organic Chemistry.

Preparation of Chloroform. SVERRE UTHEIM (Brit. Pat. 16094, 1917).—Acetaldehyde is converted instantaneously and quantitatively *into chloroform* when a 10% aqueous solution of the aldehyde is introduced into calcium hypochlorite solution at 60° to 0°. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

Alteration of Iodoform, alone or in Solution, in Direct Light. E. COMANDUCCI and G. MEDURI (*Gazzetta*, 1918, **48**, i, 38—247).—The authors have subjected solutions of *iodoform* in nineteen of the ordinary organic solvents, out of contact with the air, to the action of direct sunlight. The solution (1%) in olive oil remains unchanged after a year. In absence of solvent, iodoform undergoes very little decomposition under the above-named conditions. T. H. P.

Process of Producing Alcohols. E. I. DU PONT DE NEMOURS & Co. (Brit. Pat. 119249).—A suitable halogenated hydrocarbon, for example, a mixture of pentyl and hexyl chlorides, is passed into sodium stearate heated at 200—240° in a distillation vessel provided with a stirrer. The alkyl chloride partly reacts with the sodium stearate to form the stearic ester of an alcohol, and is partly decomposed into olefines. Arrangements are made for separating the olefines from the unchanged alkyl chloride by condensation and returning the latter to the reaction vessel. The stearic ester is cooled to 150° and treated with sufficient sodium hydroxide solution to replace the sodium which has reacted with the chloride. The mixture is again gradually heated to 200—240°, *and the alcohol liberated from the ester is distilled off* in the presence of water or steam. The sodium stearate is then ready for a fresh treatment, and may be used repeatedly until the accumulation of sodium chloride becomes excessive. J. F. B.

The Preparation of Glycols. H. HIBBERT (*Met. and Chem. Eng.*, 1918, **19**, 571—573).—A mixture of glycols in which ethylene glycol predominates may be prepared by decomposing petroleum vapours in an iron tnbe heated at about 650°, converting the product into dichloroethane, etc., purifying this compound by distillation, and treating the distillates with alkali carbonates in a closed vessel. The products thus obtained are viscous, hygroscopic liquids capable of replacing glycerol for many industrial purposes. The nitrate derivatives are much more stable at low temperatures than glyceryl trinitrate, which when frozen forms an intermediate crystalline modification capable of changing instantly into a totally different crystalline modification. Explosives pre-

pared from glycol nitrates have valuable properties not possessed by nitroglycerin explosives. [See also *J. Soc. Chem. Ind.*, December.] C. A. M.

Ether-like Compounds. II. Ether Alcohols of the Type R·O·CH$_2$·C(OH)R$_2'$. M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1917, [*A*], **10**, No. 17, 1—8; from *Chem. Zentr.*, 1918 *i*, 1144—1145).—In continuation of previous work (A., 1909 i, 869), the following ether alcohols have been prepared: *a-Methoxy-β-methylpropan-β-ol*, OMe·CH$_2$·CMe$_2$·OH, from methyl methoxyacetate and magnesium methyl iodide, b. p. 116·6°, D 0·9021; *a-ethoxy-β-methylpropan-β-ol*, b. p. 129·5°, D 0·8786, in which the hydroxyl group is readily replaced by chlorine, for example, with warm 38% hydrochloric acid, with formation of *β-chloro-a-ethoxy-β-methylpropane*, b. p. 62·5°/10 mm.; *a-propoxy-β-methylpropan-β-ol*, b. p. 149·2—150·2°, D 0·8708; *a-methoxy-β-ethylbutan-β-ol*, from magnesium ethyl iodide and methyl methoxyacetate, b. p. 157·7—158·2°, D 0·9071; *a-ethoxy-β-ethylbutan-β-ol*, b. p. 168·0—168·2°, D 0·8901, from which the highly reactive *β-chloro-a-ethoxy-β-ethylbutane* is obtained by means of hydrochloric acid; *a-propoxy-β-ethylbutan-β-ol*, b. p. 184—185°, D 0·8816; *a-methoxy-β-propylpentan-β-ol*, b. p. 192·1—192·6°, D 0·8896; *a-ethoxy-β-propylpentan-β-ol*, b. p. 202·9—203·1°, D 0·8764; *a*-n-*propoxy-β*-n-*propylpentan-β-ol*, b. p. 213·5—214·5°, D 0·8790. H. W.

Process for the Production of Methyl Sulphate. EDMOND JOHNSON BOAKE and THOMAS HAROLD DURRANS (Brit. Pat. 119250). —Methyl alcohol is treated with sulphur dioxide and chlorine, either simultaneously or successively, approximately in the proportions of one molecule of each of the gases to two molecules of the alcohol. A slight excess of sulphur dioxide should be present throughout the operation, and the liquid should be kept cool. Methyl chloride is among the gaseous products of the reaction, and may be collected after washing with an alkaline liquid. The residual liquid may be used directly as a methylating agent, or the methyl sulphate may be isolated by distillation under reduced pressure; the yield of methyl sulphate is more than 50% by weight. J. F. B.

Alkylation of Dialkyl Phosphites. T. MILOBENDZKI and T. KNOLL (*Chemik Polski*, 1917, **15**, 79—88; from *Chem. Zentr.*, 1918, *i*, 993—994).—The experiments were undertaken with the object of converting phosphorous acid or its hydrogen esters into trialkyl phosphites (compare Arbusov, A., 1907, i, 8, 174, 275).

Triethyl borate does not react with diethyl hydrogen phosphite; with the sodium salt of the latter (obtained from the acid ester and sodium in the presence of ether), small amounts of triethyl phosphite are obtained, which, however, are formed during the action of sodium (or magnesium) on the acid ester. Ethyl sulphate

and triethyl phosphite do not cause the alkylation of diethyl sodium phosphite. The sodium salts of dialkyl phosphites are decomposed by heat, diethyl sodium phosphite at 142—143°. Pure magnesium oxide does not react with dipropyl hydrogen phosphite. The dialkyl phosphites do not react with metallic magnesium when dissolved in ether, benzene, or xylene; on the other hand, dimethyl hydrogen phosphite dissolved in pyridine reacts with magnesium at the ordinary temperature, diethyl hydrogen phosphite after initial heating to 100°, dipropyl hydrogen phosphite with greater difficulty, and dibutyl hydrogen phosphite only when heated. *Magnesium diethyl phosphite* is a powder. When metallic magnesium acts on slightly warmed diethyl hydrogen phosphite, triethyl phosphite is formed in 5% yield. H. W.

Tautomerism of the Dialkyl Phosphites. T. Milobendzki (*Chemik Polski*, 1917, **15**, 89—96; from *Chem. Zentr.*, 1918, i, 994. Compare A., 1912, i, 155).—The author's previous conclusions have been somewhat modified as the result of more recent experiments. From the behaviour of the dialkyl phosphites on neutralisation, etc., the conclusion is drawn that if the esters are derivatives of quinquevalent phosphorus and of the pseudo-acids, $PHO(OR)_2$, the salts of the ester are derivatives of tervalent phosphorus, $P(OR)_2{\cdot}OMe$. The tautomerism of these substances depends on this factor. H. W.

The Distillation of some Organic Acids with Water; Measure of the Volatilisation. W. Œchsner de Coninck and A. Raynaud (*Rev. gén. Chim. pure appl.*, 1915, **18**, 134—135).—A repetition of work previously published (compare A., 1915, i, 645). The figures for acetic and *iso*butyric acids are corrected. W. G.

The Distillation of Mixtures of Water and Formic Acid. Hydrate of Formic Acid. W. Œchsner de Coninck (*Rev. gén. Chim. pure appl.*, 1916, **19**, 68. Compare A., 1915, i, 645; preceding abstract).—The composition of successive 5 c.c. portions of distillate of varying mixtures of formic acid and water indicate the existence of Roscoe's hydrate of formic acid, $4H{\cdot}CO_2H,3H_2O$, b. p. 107—108°. If such a mixture is rectified several times, it gradually loses formic acid and tends towards the hydrate, $H{\cdot}CO_2H,H_2O$. W. G.

Stereochemical Studies. III. Iodosuccinic Acids. Bror Holmberg (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 23, pp. 33; from *Chem. Zentr.*, 1918, i, 1147—1148. Compare A., 1913, i, 824; 1914, i, 139; 1917, i, 115).—The preparation of pure *l*-iodosuccinic acid is described, and its decomposition in alkaline, neutral and acid solution, and racemisation by iodides, have been further investigated.

Experiments on the velocity with which *r*-iodosuccinic acid, in aqueous and hydrochloric acid solution and as acid and normal

sodium salt (with and without addition of sodium iodide), yielc acid, lead, in conjunction with preparative experiments, to th following scheme:

$$CO_2H{\cdot}CHI{\cdot}CH_2{\cdot}CO_2H = HI + CO_2H{\cdot}CH{:}CH{\cdot}CO_2H,$$

$$CO_2H{\cdot}CHI{\cdot}CH_2{\cdot}CO_2H \rightleftharpoons HI + CO_2H{\cdot}\overline{CH{\cdot}CH_2{\cdot}CO{\cdot}O},$$ an

$$CO_2H{\cdot}\overline{CH{\cdot}CH_2{\cdot}CO{\cdot}O} + H_2O = CO_2H{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H.$$ Th formation of fumaric acid is greater the more acidic the solution its production may be due to catalysis by hydrogen ions, but it i probable that the lactonemalic acid, necessary as a step in th formation of malic acid, owes its origin preferentially or almos entirely to the anions of iodosuccinic acid (or to the correspondin salt molecules), and in this case the presence of a strong acid mus retard the formation of malic acid.

Kinetic and preparative experiments on the decomposition o iodosuccinic acid by alkali lead to the following scheme:

$$CO_2M{\cdot}CHI{\cdot}CH_2{\cdot}CO_2M + MOH = CO_2M{\cdot}CH{:}CH{\cdot}CO_2M + MI + H_2O$$

$$CO_2M{\cdot}CHI{\cdot}CH_2{\cdot}CO_2M \rightleftharpoons MI + CO_2M{\cdot}\overline{CH{\cdot}CH_2{\cdot}CO{\cdot}O},$$ an

$$CO_2M{\cdot}\overline{CH{\cdot}CH_2{\cdot}CO{\cdot}O} + MOH = CO_2M{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2M.$$ Form ation of fumaric acid is the main reaction even in strongly alkalin solution. It follows from the equations that, to secure a good yiel of malic acid, the solution must be kept as nearly neutral a possible, and, further, that it is advantageous to remove the iodin ions as they are formed. Actually, it has been found possible t obtain *silver lactonemalate*, small prisms, in a pure condition b shaking iodosuccinic acid with an excess of silver oxide, and als to isolate lactonemalic acid in the form of colourless, hygroscopi leaflets or thin plates. When iodosuccinic acid is treated witl ammoniacal silver solution, it yields fumaric and β-malamic acid the latter being formed by the action of ammonia on lactonemali acid.

l-Iodosuccinic acid, prepared from *d*-lactonemalic acid an potassium iodide, melts at 148—150° to a brownish-black liqui after previously becoming reddish-brown; it has $[\alpha]_D^{19}$ −89·8° i ethyl acetate, $[\alpha]_D^{19}$ −76·2° in alcohol, $[\alpha]_D^{19}$ −54·9° in water $[\alpha]_D^{19}$ −56·1° in 0·5*N*-sulphuric acid, $[\alpha]_D^{19}$ −35·6° as sodium hydroge salt in water, and $[\alpha]_D^{19}$ −46·5° as normal sodium salt in water.

Stereochemical experiments on the decomposition of *l*-iodo succinic acid have shown that the relationships are exactly simila to those observed with *l*-bromosuccinic acid. *d*-Lactonemalic aci is formed from *l*-iodosuccinic acid in acid, neutral, or alkaline solu tion in the presence and absence of silver salts; in acid solution *d*-lactonemalic acid yields mainly *l*-malic acid, whilst in alkalin solution it produces chiefly *d*-malic acid. The latter acid is als obtained when ammonia is employed, but probably results from *d*-β-malamic acid, the primary product of the action of ammonia on *d*-lactonemalic acid.

l-Iodosuccinic acid is far more rapidly racemised by iodine ions than is *l*-bromosuccinic acid by bromine ions. Racemisation is found to follow the simple law $C = 1/0{\cdot}4343T \cdot \log d_0/dT$, and C is proportional to the concentration of iodine ions in the solution and has the value $1/2{\cdot}45[T]$ when the solution is about 0·2 molar with respect to *l*-iodosuccinic acid. From this factor and the value of C at different concentrations of sodium and potassium iodide, the electrolytic dissociation constants of the salts is calculated to be 2·5; the conversely calculated velocity constants are in complete agreement with the experimental results. The free acid is racemised about nine times as rapidly as a normal and three times as rapidly as an acid salt. In agreement with this result, the velocity of racemisation is found to be somewhat less when the solution is more dilute with respect to acid. The mechanism of racemisation is the same as in the case of *l*-bromosuccinic acid, namely, the iodine in iodosuccinic acid is replaced by ionised iodine and the substitution is accompanied by a Walden inversion. H. W.

A Direct Rupture of the Benzene Ring without Degradation. II. H. PAULY and G. WILL (*Annalen*, 1918, **416**, 1—20. Compare A., 1914, i, 485).—The authors have already shown that when 3-nitro-*p*-cresol is warmed with concentrated sulphuric acid, hydroxylamine and β-methyl-γ-crotonolactone-γ-acetic acid (I) are formed, and they have suggested that the immediate precursor of the lactonic acid is β-methylmuconic acid (II).

$$\begin{matrix} CH{:}CMe \\ \vert \\ CO{-}{-}{-}O \end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}CO_2H \qquad \begin{matrix} CMe{:}CH{\cdot}CO_2H \\ \vert \\ CH{:}CH{\cdot}CO_2H \end{matrix}$$

(I.) (II.)

It is now shown that the latter acid can be prepared from the lactone and easily reconverted into it.

The optimum temperature for the above hydrolytic rupture of 3-nitro-*p*-cresol is 111—113°. The nitrogenous acid by-product (*ibid.*) reacts very slowly with methyl-alcoholic hydrogen chloride compared with the lactonic acid, and a separation of the acids is best effected by taking advantage of this fact. The methyl ester of the lactonic acid (now called *isoprenelactonic* or *β-methylmucolactonic* acid) has b. p. 310°/atm., and is hydrolysed by treatment with sodium methoxide solution to *methyl hydrogen β-methylmuconate* (*isoprenedicarboxylate*), which crystallises in needles, m. p. 125°. This is converted into the free *acid* (II), m. p. 71°, by hydrolysis with sodium hydroxide, and into the *dimethyl ester*, long, glistening needles, b. p. 142—143°/16 mm., m. p. 8·5°, by means of methyl sulphate. The acid resembles muconic acid in forming very sparingly soluble barium, silver, and lead salts, and the methyl ester, like isoprene, changes in the course of time into a pale, elastic polymeride. The corresponding *diamide* has m. p. 213—214°, and becomes deep bluish-green when kept molten for a few minutes; *methyl β-methylmuconamate* forms

stout prisms, m. p. 161—162°, and the vapours obtained by heating it with zinc dust give the pyrrole reactions.

The reconversion of the dicarboxylic acid into the lactonic acid can be effected by means of warm sulphuric acid, glacial acetic acid solutions of hydrogen chloride or bromide, or by melting. Similarly, the above methyl hydrogen ester yields the methyl ester of the lactonic acid when heated at 210°.

The dicarboxylic acid is most readily reduced by sodium amalgam, the product being *β-methyl-Δ^{β}-butene-αδ-dicarboxylic acid*, $CO_2H\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot CO_2H$. This was prepared previously from the lactonic acid and designated β-methyldihydromuconic acid, but the position of the ethylene linking remained to be proved. The acid, m. p. 140—141°, couples with diazonium salts, which, from analogy to glutaconic acid, shows that the double bond is in the middle of the chain. The *methyl* ester is a limpid liquid with the odour of melons, b. p. 245°/753 mm., D_4^{20} 1·0824, and yields methyl acetoacetate when its ozonide is boiled with water, this fact also attesting to the position of the ethylene linking.

The free isoprenedicarboxylic acid reacts vigorously with bromine, hydrogen bromide being evolved, but its methyl ester absorbs four atomic proportions of bromine fairly readily. The above butenedicarboxylic acid also absorbs bromine at 40—50°, giving *βγ-dibromo-β-methyladipic acid*, $CO_2H\cdot CH_2\cdot CMeBr\cdot CHBr\cdot CH_2\cdot CO_2H$, m. p. 166°, which is decomposed by boiling alcoholic potassium hydroxide, the products including isoprene and the above isoprene dicarboxylic acid. J. C. W.

Synthesis of Linamarin. EMIL FISCHER and GERDA ANGER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 203—212; from *Chem. Zentr.*, 1918, i, 1163—1164).—The synthetical methods used by Fischer and Bergmann (A., 1917, i, 657) for the preparation of mandelonitrileglucoside and sambunigrin can be extended to aliphatic hydroxy-acids; the present communication describes the synthesis of linamarin, the glucoside of acetonecyanohydrin,

$$C_6H_{11}O_5\cdot O\cdot CMe_2\cdot CN,$$

which appears to be a β-glucoside.

A mixture of acetobromoglucose and ethyl α-hydroxy*iso*butyrate is shaken with silver oxide, whereby *ethyl tetra-acetylglucosido-α-hydroxybutyrate*, $(OAc)_4C_6H_7O_5\cdot O\cdot CMe_2\cdot CO_2Et$, m. p. 114—115° (corr.), $[\alpha]_D^{20}$ −11·17° in acetone, is produced. This is converted by ammonia into *α-hydroxybutyramideglucoside*,

$$C_6H_{11}O_5\cdot O\cdot CMe_2\cdot CO\cdot NH_2,$$

needles, m. p. 166—167°, $[\alpha]_D^{18}$ −24·53° in water, which is extremely slowly hydrolysed by emulsin; in the absence of seeding material the product can only be induced to crystallise with great difficulty when prepared in this manner, and it is preferable to obtain it from the *tetra-acetyl* derivative. The latter is obtained by acetylating the crude substance obtained in the reaction just described with acetic anhydride in the presence of pyridine; it melts at

153—154° (corr.) and has $[\alpha]_D^{20}$ −21·07° in aqueous solution; it is transformed into the free amide by treatment of its methyl-alcoholic solution with ammonia. *Tetra-acetyl-linamarin*,

$$(OAc)_4C_6H_7O_5{\cdot}O{\cdot}CMe_2{\cdot}CN,$$

needles, m. p. 140—141° (corr.), $[\alpha]_D^{14}$ −10·81°, is prepared by the action of phosphoryl chloride on tetra-acetyl-α-hydroxybutyramide-glucoside at 65—68°, or by the acetylation of linamarin by acetic anhydride in the presence of pyridine. Linamarin itself is prepared by shaking an ice-cold methyl-alcoholic solution of the tetra-acetate with methyl-alcoholic ammonia; it crystallises in needles, m. p. 142—143° (corr.), $[\alpha]_D^{19}$ −29·10°. Reduction does not occur when it is boiled for a short time with Fehling's solution.

H. W.

Conversion of *l*-Glucosan into Dextrin. Amé Pictet (*Helv. Chim. Acta*, 1918, **1**, 226—230).—When kept at 240° for thirty to sixty minutes, or, better, at 180° for a few minutes in the presence of a little platinum-black as catalyst, *l*-glucosan undergoes polymerisation and is transformed into a white, amorphous *substance*, $(C_6H_{10}O_5)_4$, $[\alpha]_D$ varying from +111·9° to +106·5° in different preparations, which exhibits the characteristic properties of a dextrin and yields dextrose when warmed with dilute sulphuric acid (compare Pictet and Sarasin, this vol., i, 59; *Helv. Chim. Acta*, 1918, **1**, 87).

C. S.

Preparation of Methylamine. Hilton Ira Jones and Ruth Wheatley (*J. Amer. Chem. Soc.*, 1918, **40**, 1411—1415).—The results recently published by Werner (T., 1917, **111**, 844) have led the authors to describe certain experiments made with the object of studying the effect of reduced pressure on those organic reactions in which a gas is evolved.

Mixtures of ammonium chloride and formaldehyde were (1) slowly distilled at the ordinary pressure, (2) slowly distilled in a vacuum, (3) heated under reflux during eight hours and then distilled at the ordinary pressure, and (4) heated under reflux during four and a-half hours and then distilled in a vacuum.

The authors are led to the following conclusions: The vacuum heating under reflux and distillation decreases the amount of ammonium chloride left unused, lowers the temperature, and therefore decreases the yield of dimethylamine and more highly methylated substances, which agrees with Werner's theory, and it increases the acidity of the distillate, the loss of carbon dioxide, and the weight of methylamine produced.

The vacuum distillation, merely by removing the volatile products as well as the carbon dioxide, causes a marked increase in the weight of the distillate and the amount of ammonium chloride remaining unchanged; it causes the formation of the lowest percentage of dimethylamine, but also lowers markedly the amount of methylamine formed, and it brings about a higher percentage of esterification and gives a distillate of the highest rotatory power.

The long heating at ordinary pressure and relatively high

temperature gives the smallest percentage of distillate, the highest percentage of non-distillate residue, the highest percentage of esterification, uses up a large amount of ammonium chloride, and gives the highest degree of methylation, which means the highest percentage of dimethyl and other more highly methylated derivatives, most of which will not crystallise.

The theory advanced by Werner is correct and explains all the observed facts.

The four types of reaction agree with the principles of a larger theory which applies to all organic reactions of this type in which a gas is evolved; this is being worked out in other cases.

Methylamine is best prepared by heating under reflux in a vacuum. H. W.

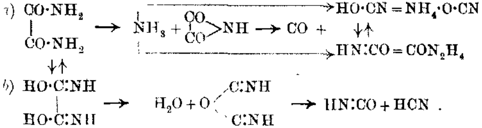
Preparation of Compounds of Carbamide and a Calcium Salt. Knoll & Co. (D.R.-P. 306804; from *Chem. Zentr.*, 1918, ii, 420).—The *compound*, $CaCl_2,4CO(NH_2)_2$, white powder, stable in air and very readily soluble in water, m. p. 158—160°, is obtained by evaporating an aqueous solution of the components in the required proportion to dryness, or of an alcoholic solution to crystallisation; it is useful for subcutaneous injection in hay fever and asthma, since it does not give rise to pain as with calcium chloride alone. The compounds of calcium chloride with one, two, or three molecules of carbamide are hygroscopic, whilst those with more than four molecules have a too low content of calcium chloride for pharmaceutical purposes. H. W.

Constitution of Carbamides. VII. The Mechanism of the Synthesis of Urea from the Interaction of Carbonyl Chloride and Ammonia. VIII. Formation of Urea and Biuret from Oxamide. Emil Alphonse Werner (T., 1918, **113**, 694—701).—VII. The production of urea by the action of carbonyl chloride on ammonia is usually regarded as evidence of the "carbamide" structure for urea. It is now shown, however, that considerable quantities of biuret, ammelide, and cyanuric acid, and traces of cyamelide, are formed as well, biuret being observed for the first time. Taking these by-products into consideration, the "synthesis" really affords evidence in support of the view that urea is the product of the union of ammonia and cyanic acid in its keto-form. The mechanism of the reactions is expressed as follows:

$$COCl_2 + 2NH_3 \longrightarrow NH_2\cdot COCl + NH_4Cl \longrightarrow HCl + \left\{ \begin{array}{l} HO\cdot CN \longrightarrow \text{Cyamelide} \\ \quad \downarrow\uparrow \qquad\qquad \text{by polymerisation} \\ HN{:}CO \longrightarrow \text{Cyanuric acid} \end{array} \right.$$

Urea then arises from the union of ammonia and HN:CO, biuret from the interaction of urea and cyanic acid, and ammelide from the biuret and cyanic acid.

VIII. [With George Kingsford Carpenter.]—When oxamide s heated to a temperature sufficient to effect complete volatilisa-ion, ammonium cyanate, urea, and biuret are found in the ublimate, and ammonia, water, carbon monoxide, and hydrogen yanide are evolved. The decomposition is represented thus:



J. C. W.

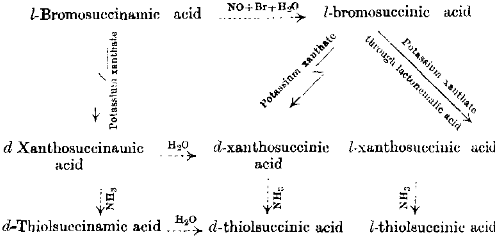
Stereochemical Studies. III. Xantho- and Thiol-β-succinnamic Acids. B. Holmberg and K. J. Lenander (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 17, pp. 26; from *Chem. Zentr.*, 918, i, 1145—1146. Compare A., 1917, i, 115).—Previous in-estigations (A., 1914, i, 140) have shown that, according to the xperimental conditions, a lævo- or dextro-rotatory xanthosuccinic cid can be obtained by the action of potassium xanthate on salts f *l*-bromosuccinic acid, whilst salts of *l*-β-bromosuccinamic acid nly yield a dextrorotatory xanthosuccinamic acid of constant pecific rotation when treated with xanthates. It further appears hat xanthosuccinic acid is formed from *l*-bromosuccinic acid by irect substitution (*d*-acid) and by addition of xanthate to the rimarily formed *d*-lactonemalic acid (*l*-acid), and that change of onfiguration occurs with direct substitution. The reaction etween xanthates and salts of *l*-bromosuccinamic acid can only be case of direct substitution, and opposite configurations must there-ore be ascribed to *l*-bromosuccinamic acid and *d*-xanthosuccinamic cid. To test this point, the reaction between potassium xanthate nd salts of *l*-bromosuccinamic acid has been thoroughly investi-ated, and the relationships between the active xantho- and thiol-uccinic acids and the corresponding active β-substituted succinamic cids have been established.

Kinetic investigations of the action of potassium xanthate on he salts of *l*-bromosuccinamic acid lead to velocity constants of the econd order which diminish slightly as the action proceeds, and re rather greater with barium and strontium than with sodium nd potassium salts. As the reaction proceeds slowly, so that the romosuccinamic acid may be, in part, decomposed by the water thus explaining the slight decrease in the velocity constants), it ppears that the xanthosuccinamic acid is entirely formed in ccordance with the scheme:

$$O_2M\cdot CHBr\cdot CH_2\cdot CO\cdot NH_2 + KS\cdot CS\cdot OEt = KBr + CO_2M\cdot CH(S\cdot CS\cdot OEt)\cdot CH_2\cdot CO\cdot NH_2,$$

nd that the reaction is only slightly accelerated by metallic ions. -Thiolsuccinic acid is formed from *d*-thiolsuccinamic acid

by hydrolysis in acid or alkaline solution. The mutual relationships of the individual acids are shown in the following scheme, in which the dotted arrows denote reactions which occur without affecting the asymmetric carbon atom, whilst straight and zig-zag arrows show actions taking place without and with change of configuration respectively:



r-β-Xanthosuccinamic acid forms silky platelets, m. p. 125—126° (*decomp.*). The *corresponding d-acid is prepared by the action of* potassium xanthate on potassium, sodium, or strontium *l*-bromosuccinamates; after exhaustive purification, it has m. p. 134—135° (decomp.), $[\alpha]_D^{18}$ +53·1° (c=2·769) and $[\alpha]_D^{18}$ +55·5° (c=6·597) in acetone, $[\alpha]_D^{17}$ +66·0° in ethyl acetate; it is slowly racemised and slightly decomposed when its solution in ethyl acetate is heated. l-β-*Xanthosuccinamic acid* is obtained by resolution of the inactive acid with *d*-phenethylamine; it has m. p. 134—135° (decomp.), $[\alpha]_D^{19}$ −53·4° (c=4·055) in acetone.

r-β-*Thiolsuccinamic acid*, prepared by the action of ammonia on *r*-xanthosuccinamic acid or by mixture of equal weights of the components, crystallises in plates, m. p. 103—104° (decomp.). The corresponding d-*acid*, small, colourless prisms, m. p. 125—126° (decomp.), has $[\alpha]_D^{18}$ +82·5° in acetone, $[\alpha]_D^{18}$ +58·7° in water, whilst the *sodium* salt has $[\alpha]_D^{18}$ +36·8° in water; the *ammonium* salt forms colourless plates or thin prisms, $[\alpha]_D^{19}$ +33·6° in water. l-β-*Thiolsuccinamic acid* has m. p. 125—126° (decomp.), $[\alpha]_D^{18}$ −82·9° in acetone. H. W.

Epimeric Hexosamic Acids. P. A. Levene (*J. Biol. Chem.*, 1918, **36**, 73—87. Compare Levene and La Forge, A., 1915, i, 782, 944).—The author attempts to determine the position of the amino-group in various amino-sugars by comparing the properties *of pairs of epimeric hexonic acids with corresponding pairs of* hexosamic acids, especially with regard to the equilibrium of the two epimerides formed on the synthesis of the hexoic acids from the corresponding pentoses and the direction of the rotation of the α-carbon atom in corresponding pairs of epimerides. Three pairs

of epimeric α-hexosamic acids have been prepared and examined; two arabinohexosamic acids, two lyxohexosamic acids, and two xylohexosamic acids. Of the first pair, one is prepared by the oxidation of chitosamine (glucosamine) and the other by the action of pyridine on chitosamic (glucosamic) acid. *Epichitosamolactone hydrochloride*, $C_6H_{12}O_5NCl$, is prepared by treating the raw product, obtained by the action of pyridine on chitosamic acid, with alcohol and benzaldehyde, and then with gaseous hydrogen chloride. The addition of the benzaldehyde has for its purpose the conversion of the chitosamic acid into the benzylidene compound of its ethyl ester, which remains in solution. The lactone is precipitated by ether and recrystallised from methyl alcohol. It crystallises in prismatic needles, m. p. 203° (decomp.), $[\alpha]_D^{20}$ +45°. On dissolving in water rendered alkaline with barium hydroxide, the lactone is converted into the free *epichitosamic acid*, $C_6H_{13}O_6N$, colourless, prismatic needles, m. p. 198° (decomp.), $[\alpha]_D^{20}$ initial −10°, equilibrium +39°. The rotation of chitosamic acid being −15·02°, that of the α-carbon atom is {10·0−(−15·02)}/2 = 12·51°.

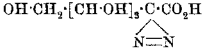
A mixture of chondrosamic and epichondrosamic acids is obtained by the action of hydrocyanic acid on lyxose in the presence of ammonia. The reaction is very capricious, the result obtained depending on the temperature and the duration of the reaction, the optimum values for which have to be determined empirically for each sugar. When successful, the yield amounts to 50% of the theoretical quantity, but often, with the best care, it falls to 25%, or even less. The mixture of epimerides can be separated by fractional crystallisation from dilute methyl alcohol; d-*chondrosamic acid*, $C_6H_{13}O_6N$, has m. p. 206° (decomp.) and $[\alpha]_D^{20}$ −17·0°, whilst d-*epichondrosamic acid* has $[\alpha]_D^{20}$ +8·0°, the numerical value of the α-carbon atom being again 12·5°.

d-Xylohexosamic acid, as prepared by Levene and La Forge (*loc. cit.*), was not pure, but consisted of a mixture of the two epimerides. It has now been prepared synthetically from xylose by the action of hydrocyanic acid, the product being fractionated in a similar manner to that indicated in the case of the chondrosamic acids. d-d-*Xylohexosamic acid*, $C_6H_{13}O_5N$, has m. p. 224° (decomp.) and $[\alpha]_D^{20}$ +14°, whilst d-l-*xylohexosamic acid* has m. p. 200° (decomp.) and $[\alpha]_D^{20}$ −11·0°, the value for the rotation of the α-carbon atom being 12·5°, as before. Both epimerides were converted into lactones. d-d-*Xylohexosamolactone hydrochloride*, $C_6H_{12}O_5NCl$, has m. p. 205° (decomp.), and on treatment with barium hydroxide is reconverted into the parent acid. The other lactone was obtained in the form of its benzaldehyde derivative by treating *d-l*-hexosamic acid in alcoholic solution with benzaldehyde and passing in hydrogen chloride. Crystallisation occurs spontaneously. After recrystallisation, *benzylidene*-d-l-*xylohexosamic-lactone hydrochloride*, $C_{13}H_{15}O_5N,HCl$, melts at 206° (decomp.) and has a rotation of $[\alpha]_D^{20}$ −60·5°. It is readily transformed into the parent acid by means of barium hydroxide.

After comparison of the rotations of these hexosamic acids with the corresponding hexonic acids, the authors suggest probable configurations for these three pairs of epimeric acids.

H. W. B.

Action of Nitrous Acid on Epimeric Hexosamic Acids. P. A. LEVENE (*J. Biol. Chem.*, 1918, **36**, 89—94. Compare preceding abstract).—Levene and La Forge (A., 1915, i, 786) have shown that the replacement of the amino-group by hydroxyl in amino-sugars and their derivatives probably takes place with the intermediate formation of a diazo-compound. Accepting for the structure of the diazo-compound the expression



it appears that each of a pair of epimerides should give one and the same diazo-compound, and hence one and the same deaminised acid. However, by the action of nitrous acid on the three pairs of epimerides described in the preceding abstract, six different acids are produced. The deaminisation is brought about in each case by dissolving the acid in dilute hydrochloric acid and treating with silver nitrite. The products from the different amino-acids are then treated in various ways. Chitosamic and epichitosamic acids after deaminisation are reduced, yielding *d*-anhydrogulonic and *d*-anhydromannonic acids respectively; chondrosamic and epichondrosamic acids, after deaminisation and oxidation, give *d*-anhydromucic and *d*-anhydrotalomucic acids, whilst *d*-*d*-xylohexosamic and *d*-*l*-xylohexosamic acids on similar treatment yield *d*-anhydroidosaccharic and *l*-anhydrosaccharic acids respectively. It is further noted that whereas *d*-xylohexosamic acid and its lactone give *d*-anhydroidosaccharic and *l*-anhydrosaccharic acids respectively, epichitosamic acid and its lactone form the same *d*-anhydromannonic acid. Thus, whilst in the first instance a Walden inversion takes place, in either the acid or the lactone, in the second the inversion occurs in neither or in both. H. W. B.

Direct Transformation of Acid Chlorides into Nitriles by Catalysts. ALPH. MAILHE (*Bull. Soc. chim.*, 1918, [iv], **23**, 380—381).—Acid chlorides may be converted directly into the corresponding nitriles by passing their vapours, along with ammonia, over aluminium oxide at 490—500°. Excellent yields were obtained from benzoyl, *iso*valeryl, *iso*butyryl, and propionyl chlorides. W. G.

[Reactions of] Cyanogen Products. V. MACRI (*Boll. chim. farm.*, 1918, **57**, 261—265).—The author has purified the crude carbonylferrocyanide obtained from the wash-waters of the Laming mixture, and has subjected the pure product, and also alkali cyanide, thiocyanate, and ferrocyanide, to the action of a number

of reagents; the results are tabulated. The carbonylferrocyanide is a highly stable compound. T. H. P.

Chromithiocyanic Acid and Chromithiocyanates. GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 442—445).—In order to obtain salts of bivalent metals with chromithiocyanic acid, the author has made use of hexamethylenetetramine, which combines with the hydrates of the salts in solution to form stable and insoluble, wine-red double compounds, these being isomorphous and of the general formula $M''_3[Cr(SCN)_6]_2,10H_2O,3C_6H_{12}N_4$. A concentrated solution of the hexamethylenetetramine was added to a solution containing either ammonium chromithiocyanate and a soluble salt of the metal in question, or barium chromithiocyanate and the sulphate of the metal. In this way, the compounds of hexamethylenetetramine with the chromithiocyanates of manganese, cobalt, nickel, magnesium, calcium, zinc, cadmium, and strontium were prepared, the first five being analysed.

Chromithiocyanic acid, $H_3Cr(SCN)_6$, may be prepared by treating a concentrated solution of the ammonium or barium salt (1 mol.) with 10% sulphuric acid (3 mols.) solution in the cold. The liquid is extracted repeatedly with ether until the solvent is no longer coloured red, the ethereal solution being washed with water until all sulphuric acid is removed, and dried with anhydrous sodium sulphate. After evaporation of the ether, the chromithiocyanic acid remains as a bright red oil which does not solidify in a mixture of ice and salt, and does not decompose below about 40°, but at higher temperatures emits hydrocyanic acid and vapours of alliaceous odour. It is a moderately energetic acid almost comparable with the mineral acids; thus, a solution of normal concentration attacks metals, for instance, zinc turnings, in the cold with evolution of hydrogen. The electrical conductivities of its solutions at 25° are a little greater than those of equivalent solutions of phosphoric acid. T. H. P.

Preparation of Ethanoltrialkylarsonium Hydroxides and their Salts. CHEMISCHE WERKE GRENZACH (D.R.-P., 305772; from *Chem. Zentr.*, 1918, ii, 83).—Arsonium compounds of the choline type are prepared by the action of glycol halogenhydrins on trialkylarsines; they possess valuable therapeutic properties.

Trimethylethanolarsonium hydrochloride, $C_5H_{14}OAsCl$, very hygroscopic, prismatic crystals, m. p. 218—220°, is produced from glycol chlorohydrin and trimethylarsine at 120—125°; the free *base* forms a viscous mass which slowly crystallises and reacts strongly alkaline. Hydrogen sulphide does not give a precipitate with the aqueous solution of the hydrochloride; with mercuric chloride, a crystalline double salt is formed. Mayer's reagent gives a faint white, potassium iodide and iodine a dirty brown precipitate. Phosphotungstic acid gives a copious white precipitate. The *hydriodide* forms long, hygroscopic needles; the *sulphate*, m. p. 240°, is hygroscopic. The *di-iodosalicylate*, m. p. 140°, is stable in the

air. The *picrate*, *gold* and *platinum* salts, and the *picrolonate* are also described. *Trimethylethanolarsonium hydrobromide* forms thick, hygroscopic prisms, m. p. 219°. *Triethylethanolarsonium hydrochloride* consists of slender, very hygroscopic needles; the free *base* forms a viscous mass. The *di-iodosalicylate*, m. p. 118°, is stable in the air, as is also the *triborate*. The *picrate* has m. p. 152°. H. W.

Unsaturation and Molecular Compound Formation. O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1918, **40**, 1561—1573).—Freezing-point determinations of mixtures of benzene, toluene, ethylbenzene, mesitylene, and acetylene, respectively, with hydrogen bromide have been made, and the freezing-point curves constructed with the object of ascertaining the influence of structure on the formation of additive compounds. It is shown that acetylene and benzene do not form molecular compounds with hydrogen bromide at low temperatures. The existence of the compound, $2C_6H_5Me,HBr$, m. p. $-86·5°$, has been verified, and the existence of compounds, C_6H_5Et,HBr, m. p. $-105·5°$, $2C_6H_5Et,HBr$, m. p. $-103·8°$, and $C_6H_3Me_3,HBr$, m. p. $-61°$, demonstrated. J. F. S.

Intramolecular Migrations of the Phenyl Group. P. J. MONTAGNE (*Chem. Weekblad*, 1918, **15**, 1195—1204).—A lecture delivered before the Chemical Society of Leyden. A. J. W.

The Freezing-point Curve of Mixtures of Toluene-*o*- and -*p*-sulphonamides. Composition of Mixtures of Toluene-*o*- and -*p*-sulphonic Acids. PHYLLIS VIOLET MCKIE (T., 1918, **113**, 799—803).—The freezing-point curve of mixtures of toluene-*o*- and -*p*-sulphonamides is a simple one, giving a well-defined eutectic, m. p. 110·25°, containing 61·25% of the *p*-sulphonamide. The *o*-amide has m. p. 156·3° and the *p*-amide m. p. 137·45°. This curve can be used to determine the composition of mixtures of the respective acids by converting them into the amides through the chlorides, and determining the melting point of the resulting mixture of amides. T. S. P.

Preparation of Hydrogenated Compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 306724; additional to D.R.-P. 305347; from *Chem. Zentr.*, 1918, ii, 420).—Other aromatic isocyclic and heterocyclic compounds, in addition to bases, can be reduced with alkali or alkaline earth metals and alcohol in the presence of an indifferent solvent. The process is easily regulated and can be stopped at any point by withholding further addition of alcohol. Thus, tetrahydronaphthalene is obtained from naphthalene, sodium, and alcohol in the presence of solvent naphtha at 140—145°, and *tetrahydrodiphenyl*, b. p. 247—249°, 115—118°/10—12 mm., from diphenyl, sodium, alcohol, and solvent naphtha at 140—150°. Acenaphthene yields tetrahydroacenaphthene. H. W.

Preparation of Certain Organic Stanno- and Stanni-chlorides. John Gerald Frederick Druce (T., 1918, **113**, 715—718).—Diethylamine stannochloride, the stanno- and stanni-chlorides of *o*-toluidine, methylaniline, *m*- and *p*-phenylenediamine and benzylamine, and *p*-methylbenzylamine stannochloride have been prepared from hydrochloric acid solutions of the component haloids. J. C. W.

Preparation and Properties of Aniline Stannichloride. J. G. F. Druce (*Chem. News*, 1918, **117**, 346—348).—A crystalline hydrate of aniline stannichloride, $(NH_2Ph)_2,H_2SnCl_6,3H_2O$, is obtained in pale pink tablets by crystallising a mixture of two molecules of aniline and one molecule of stannic chloride from hydrochloric acid. This compound loses water on heating, with the formation of an amorphous residue which melts at 292° to a dark brown liquid. The anhydrous compound is best prepared by adding 80 c.c. of concentrated hydrochloric acid to a mixture of 15 grams of tin and 10 grams of nitrobenzene, heating until the nitro-compound has been reduced, and then cooling. The cold, solid mass is dissolved in 200 c.c. of warm diluted hydrochloric acid, and 18 grams of aniline added. On cooling, an almost quantitative yield of the anhydrous aniline stannichloride is obtained. A number of other methods of preparation are given. It is a colourless, crystalline compound, m. p. 293° (slight decomp.). It dissolves in water to the extent of 28 grams in 100 c.c. at 16°. On keeping, it darkens. This compound may be used in the preparation of quinoline instead of a mixture of aniline and nitrobenzene. J. F. S.

Influence of Temperature on the Decomposition of Sodium Phenoxide and Tolyloxides by Carbon Dioxide. G. J. Denbigh (*J. Soc. Chem. Ind.*, 1918, **37**, 306—307T).—The liberation of phenol and the cresols from solution in sodium hydroxide by means of carbon dioxide has been studied under various conditions of temperature. The author is led to the conclusion that all three cresols are more easily liberated than phenol, and, further, that they only differ slightly among themselves in this respect, *m*-cresol being most readily and *o*-cresol least easily set free. In the case of both phenol and cresols, the decomposition is more complete when warm, and the rate increases more rapidly with all the cresols than with phenol.

Attempts have been made to separate phenol from cresol by fractional decomposition; the work is being continued in this direction. H. W.

Tartaric Amides and Imides. II. Luigi Casale (*Gazzetta*, 1918, **48**, i. 114—120).—p-*Aminophenol hydrogen* d-*tartrate*, $CO_2H\cdot[CH\cdot OH]_2\cdot CO_2H,NH_2\cdot C_6H_4\cdot OH$, forms colourless scales, m. p. 232° (corr.).

p-*Hydroxyphenyltartrimide*, $\begin{matrix}CH(OH)\cdot CO\\CH(OH)\cdot CO\end{matrix}\!\!>N\cdot C_6H_4\cdot OH$, obtained

by heating the above salt in a vacuum at about 200°, forms long, silky, colourless needles, m. p. 299° (corr.; decomp.), $[\alpha]_D^{20}$ +119·64°, $[\alpha]_D^{15}$ +120·7°; its solubility in methyl alcohol at 13° is 2·913%.

d-*Hydroxyphenyltartramide*,

$OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NH_2$,

forms white needles, m. p. 227° (corr.), $[\alpha]_D^{15}$ +154°; its solubility in methyl alcohol at 15° is 1·58%.

d-*Phenylhydroxyphenyltartramide*,

$OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NHPh$,

prepared by heating the preceding compound in presence of aniline, forms silky, white needles, m. p. 253° (corr.); its solubility in methyl alcohol at 15° is 1·582%.

p-*Hydroxyphenyltartramic acid*,

$OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$,

forms white plates, m. p. 218° (corr.), $[\alpha]_D^{14}$ +108·3°, and, when heated slowly, is transformed into the imide without melting; its solubility in water at 14° is 4·215%. The *methyl*, m. p. 206° (corr.; decomp.), $[\alpha]_D^{15}$ +109·5°, *ethyl*, m. p. 118° (corr.), $[\alpha]_D^{15}$ +106·1°, and *propyl* esters, m. p. 133° (corr.), $[\alpha]_D^{15}$ +103·8°, were prepared.

T. H. P.

Benzoylation of some Hydroxyl or Amino-Aromatic Compounds. FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1918, **1**, 205—209).—A mixture of the substance and benzoyl chloride is treated with two or three drops of concentrated sulphuric acid, and, if necessary, warmed for a short time on the water-bath. The method succeeds in benzoylating substances, which are unaffected by the usual methods of benzoylation. Thus, 2:3:5-trinitro-*p*-anisidine yields a *benzoyl* derivative, colourless needles, m. p. 205°, resorcinol yields a mixture of the mono- and di-benzoates, alizarin yields the *dibenzoate*, $C_{14}H_6O_2(OBz)_2$, yellow needles, m. p. 210—211°, 2:4-dinitroaniline yields 2:4-dinitrobenzanilide, m. p. 201—202°, 1-aminoanthraquinone yields the benzoyl derivative, m. p. 246°, and 2-aminoanthraquinone yields a *benzoyl* derivative, yellow prisms, m. p. 227°, sintering at 195°. C. S.

Preparation of Glycollyl-*p*-aminophenyl Ethers. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 306938; from *Chem. Zentr.*, 1918, ii, 420—421).—Glycollyl-*p*-aminophenyl ether is obtained in excellent yield and in a high state of purity by heating *p*-aminophenyl ether with the glycollic anhydrides; the latter are considered to comprise glycollide, m. p. 86°, polyglycollide, m. p. 223°, and the product formed when glycollic acid is heated at about 200—250°, which consists of a crystalline powder insoluble in water, by which it is slowly converted into glycollic acid. Esters of glycollic acid can be used in place of the anhydrides. *Glycollyl*-p-*phenetidine* forms colourless crystals, m. p. 153°; *glycollyl*-p-*anisidine* has m. p. 101°. H. W.

The Bromination of some Derivatives of Veratrole. JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1918, **113**, 782—790. Compare T., 1917, **111**, 69, 220; this vol., i, 22).—The action of bromine on the two isomeric acetylaminoveratroles and the three acetylaminoveratric acids has been investigated. The bromine always entered the nucleus in the *para*-position with respect to the acetylamino-group, except in the case of 6-acetylaminoveratric acid, when, this position being already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole. Only in one case was the formation of an isomeride detected, namely, when 3-acetylaminoveratrole was brominated under special conditions; this isomeride could not be definitely orientated.

In view of the fact that the formation of the bromoamide always preceded substitution in the nucleus, which was therefore indirect, these experiments cannot claim to throw any light on the mechanism of nitration of this type of substance.

For experimental details, the original paper must be consulted.

H. W.

Sulphur Aryl Chlorides. IV. 4-Chloro-2-nitrochlorothiolbenzene (*p*-Chloro-*o*-nitrophenyl Sulphur Chloride). Conversion into Thiazine Derivatives. TH. ZINCKE and JOHANNA BAEUMER (*Annalen*, 1918, **416**, 86—112. Compare this vol., i, 385).—2:5-Dichloronitrobenzene is converted by Wohlfahrt's method (A., 1903, i, 203) into 4:4′-*dichloro*-2:2′-*dinitrodiphenyl disulphide*, which crystallises in glistening, yellow leaflets, m. p. 212°, and is transformed by treatment with chlorine in chloroform into 4-*chloro-2-nitrochlorothiolbenzene*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}SCl,$$

which forms golden-yellow needles, m. p. 98°. The latter is a highly reactive substance, and many of its derivatives are now described. The corresponding *bromothiol* forms brownish-yellow needles, m. p. 111°.

The chlorothiol reacts with methyl alcohol to give different products under different conditions; when boiled with 75% alcohol, it yields the above disulphide, which is insoluble in the hot liquid, the sulphinic acid (below), which is soluble even in the cold, and 4-*chloro-2-aminobenzenesulphonic acid*, decomp. above 250°, which crystallises on cooling the filtrate. Potassium cyanide reacts with a hot acetic acid solution of the chlorothiol to give 4-*chloro-2-nitrophenyl thiocyanate*, pale yellow needles, m. p. 116—117°. On shaking with water and glass beads for several hours, the product is 4-*chloro-2-nitrothiophenyl oxide*, $O(S{\cdot}C_6H_3Cl{\cdot}NO_2)_2$, which crystallises in yellow tablets, blackens at 115—116°, explodes if heated rapidly, and closely resembles *o*-nitrothiophenyl oxide in its reactions (A., 1912, i, 763). Esters of the sulphinous acid, $NO_2{\cdot}C_6H_3Cl{\cdot}S{\cdot}OR$, are obtained by the action of alcoholic or ethereal solutions of the sodium alkyl (or aryl) oxides; the *methyl* ester forms golden leaflets, m. p. 111—112°; the *ethyl* ester crystal-

lises in yellow needles, m. p. 73—74°; the *phenyl* ester forms nodules of stout, yellow needles, m. p. 75°.

4-*Chloro-2-nitrobenzenesulphinic acid*, $NO_2 \cdot C_6H_3Cl \cdot SO_2H$, slender, glistening leaflets, m. p. 127° (decomp.), is prepared by shaking the chlorothiol with 2*N*-sodium hydroxide and acidifying the filtrate. Its silver salt reacts with methyl iodide to form the *methyl* ester, m. p. 143°, and with the chlorothiol to give 4 : 4′-*dichloro-2 : 2′-dinitrodiphenyl disulphoxide*, $S_2O_2(C_6H_3Cl \cdot NO_2)_2$, needles, m. p. 145°.

The chlorothiol reacts with ammonia in chloroform solution to give 4-*chloro-2-nitrophenylthiolamine*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot NH_2$, which crystallises in glistening, yellow leaflets, m. p. 126—127°, and resembles *o*-nitrophenylthiolamine in its reactions (*ibid.*). It forms a *benzylidene* compound, long, yellow needles, m. p. 161°, and when boiled with 50% acetic acid, changes into 4 : 4′-*dichloro-2 : 2′-dinitrodiphenyldithiolamine*, $NH(S \cdot C_6H_3Cl \cdot NO_2)_2$, slender, pale yellow needles, m. p. 210° (decomp.).

Towards phenols, the chlorothiol behaves like a diazonium chloride; phenol gives 4-*chloro-2-nitro-4′-hydroxydiphenyl sulphide*, yellow needles, m. p. 130°; α-naphthol forms 4-*chloro-2-nitrophenyl-2′-α-hydroxynaphthyl sulphide*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot C_{10}H_6 \cdot OH$, small, yellow tablets, m. p. 154—155°; β-naphthol yields a *sulphide* which crystallises in orange-yellow needles, m. p. 185°.

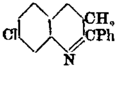
The chlorothiol also condenses with ketones. Acetone yields 4-*chloro-2-nitrophenylthiolacetone*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot CH_2 \cdot COMe$, yellow leaflets or broad needles, m. p. 114—115°; acetophenone gives *phenyl 4-chloro-2-nitrophenylthiolmethyl ketone*, pale yellow needles, m. p. 155°, which is oxidised by nitric acid to benzaldehyde and 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl disulphide (above); ethyl acetoacetate or its copper compound forms *ethyl 4-chloro-2-nitrophenylthiolacetoacetate*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot CHAc \cdot CO_2Et$, pale yellow tablets, m. p. 129—130°, decomp. 170°; acetylacetone yields *diacetyl-4-chloro-2-nitrophenylthiolmethane*,

$$NO_2 \cdot C_6H_3Cl \cdot S \cdot CH(COMe)_2,$$

brilliant yellow, large needles, m. p. 116—117°. The acetophenone and acetoacetic ester compounds may be oxidised by perhydrol or chromic acid to *sulphoxides*; the *compound*,

$$NO_2 \cdot C_6H_3Cl \cdot SO \cdot CH_2Bz,$$

forms pale yellow needles, m. p. 144°, and the *compound*, $NO_2 \cdot C_6H_3Cl \cdot SO \cdot CHAc \cdot CO_2Et$, stout, yellow tablets, m. p. 111°. They may also be reduced by means of stannous chloride, but the products are thiazine derivatives, and not amines. They separate as stannichlorides. 6-*Chloro-3-phenyl-1 : 4-benzothiazine* (annexed formula) crystallises in pale yellow, glistening tablets, m. p. 64°, and forms orange or red salts with the mineral acids, these being decomposed by water. The thiazine changes in a few days into a mixture of two compounds with the m. p.'s 178° and 241°; the change also proceeds in solution, acetic acid favouring the compound with



the higher m. p. and chloroform the other. The constitution is elucidated by the fact that the thiazine may be synthesised by the action of ω-bromoacetophenone on 4-chloro-2-aminothiophenol. *Ethyl* 6-*chloro*-3-*methyl*-1 : 4-*benzothiazine*-2-*carboxylate* crystallises in glistening, orange-red tablets or stout needles, m. p. 177—178°.
J. C. W.

Action of Formic Acid on the Triarylcarbinols. ADOLPHE KOVACHE (*Ann. Chim.*, 1918, [ix], **10**, 184—248).—A more detailed account of work already published (compare Guyot and Kovache, A., 1912, i, 186, 972; 1913, i, 647). W. G.

The Constitution of Dypnopinacone and its Derivatives. MAURICE DELACRE (*Ann. Chim.*, 1918, [ix], **10**, 101—137).—A theoretical discussion of work already published (compare A., 1914, i, 1068; 1916, i, 479). W. G.

The Hydrates and Alcoholates of Calcium Benzoate. FREDERICK STANBRIDGE (T., 1918, **113**, 808—816).—Anhydrous calcium benzoate combines with alcohol to form a *dialcoholate*, $(C_6H_5\cdot CO_2)_2Ca,2C_2H_6O$, which crystallises in very small, transparent needles, and is very unstable.

When calcium benzoate trihydrate is treated with 95% (vol.) alcohol there is no action, but with 97% (vol.) alcohol the trihydrate is rapidly acted on. By the thermometric method, using 92·85% (weight) alcohol, it is found that the trihydrate rapidly changes at 35·5° into silky, oblong plates consisting of the monohydrate, $(C_6H_5\cdot CO_2)_2Ca,H_2O$.

The solubility curve of calcium benzoate was determined, and it is shown that the trihydrate exists between −0·37°, the cryohydric point, and 84·7°. The latter temperature is a transition temperature, above which the monohydrate is probably the solid phase, although it could not be definitely isolated. The saturated solutions at the cryohydric and transition temperatures contain 2·22 and 7·62 grams of calcium benzoate, respectively, per 100 grams of water. Metastable portions of the solubility curves for both the trihydrate and monohydrate were obtained. The freezing-point curve of solutions of calcium benzoate of various strengths was also determined. T. S. P.

Preparation of Solutions of Mercuric Benzoate by means of Sodium Chloride. MARCEL DELÉPINE (*Bull. Sci. Pharmacol.*, 1917, **24**, 329—335; from *Chem. Zentr.*, 1918, i, 853).—Solutions of mercuric benzoate for subcutaneous injection, prepared by means of sodium chloride, contain a chlorine compound of mercury as the active constituent, and are therefore more simply obtained from the corresponding quantities of mercuric chloride, sodium benzoate, and sodium chloride, since in both cases the same equilibrium is reached in the solutions in consequence of the action of the sodium chloride on the mercuric benzoate. This view, first put forward by Varet on thermochemical grounds, is upheld by the fact that the two solutions contain the same quantity of mercury after being

shaken with ether. Solutions containing unchanged mercuric benzoate can be prepared by means of ammonium benzoate and ammonia; acetates and nitrates also have no action on the benzoate.

Mercuric benzoate, $(PhCO_2)_2Hg,H_2O$, is obtained by treating mercuric nitrate (225 grams in 1 litre of water) with sodium acetate (100 grams in 1 litre of water) and sodium benzoate (144 grams in 2 litres of water). C. S.

Phthalic Acid Derivatives: Constitution and Colour. XIV. Some Derivatives of Tetrabromophthalimide. DAVID S. PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1415—1425).—In continuation of previous work, a series of derivatives of tetrabromophthalimide has been prepared (compare this vol., i, 167). In general, their properties closely resemble those of the tetrachloro- and tetraiodo-analogues, with the differences that might be expected from the substitution of bromine for chlorine or iodine.

Tetrabromophthalic anhydride, m. p. 279·5—280·5° (corr.), is prepared by the action of bromine on a hot solution of phthalic anhydride in fuming sulphuric acid in the presence of iodine; with dimethylaniline, it forms an additive *product*, $C_8O_3Br_4{\cdot}NMe_2Ph$, dark red crystals. *Tetrabromophthalimide*, small, yellow blades which decompose at about 300° and do not melt at 380°, is obtained by boiling a solution of the anhydride in nitrobenzene with formamide; it gives no colour when moistened with dimethylaniline.

The following series of derivatives was prepared by boiling a solution of the anhydride in glacial acetic acid with the requisite amine: *tetrabromophthalanil*, colourless plates with faint green cast, m. p. 279—280° (corr.): it gives a slight orange colour with dimethylaniline; *tetrabromophthal*-o-*tolil*, small, colourless plates, m. p. 291—293° (corr.); *tetrabromophthal*-m-*tolil*, almost colourless, glistening plates, m. p. 273·5—274·5° (corr.); *tetrabromophthal*-p-*tolil*, pale yellow needles, m. p. 280—280·5° (corr.), which crystallises from xylene with $\frac{1}{4}$ molecule of solvent of crystallisation; *tetrabromophthal*-o-*nitroanil*, fine, hair-like crystals, m. p. 289—298·5° (corr.; decomp.): it gives an additive *product* with dimethylaniline, crystallising in red, quadrilateral plates; *tetrabromophthal*-m-*nitroanil*, slender plates, m. p. 301·5—303° (corr.); *tetrabromophthal*-p-*nitroanil*, colourless needles, m. p. 331—331·5° (corr.); *tetrabromophthal*-p-*hydroxyanil*, short, yellow needles, m. p. 296—308° (corr.; decomp.): it separates from xylene with $\frac{1}{2}C_6H_4Me_2$; it gives an additive *compound* with dimethylaniline; *tetrabromophthal*-p-*acetylaminoanil*, minute, colourless needles, decomposing without melting at 381° (corr.); *tetrabromophthal*-p-*bromoanil*, minute blades with faint green colour, which do not melt at 380° (corr.); *tetrabromophthal*-2:4-*dibromoanil*, colourless prisms, m. p. 296—298·5° (corr.); *tetrabromophthal*-2:6-*dibromoanil*, nearly colourless, hexagonal crystals, m. p. 323·5—327° (corr.); *tetrabromophthal*-2:4:6-*tribromoanil*, colourless, diamond-shaped plates, m. p. 297—298° (corr.) (in these two cases, zinc

chloride is used as condensing agent); *tetrabromophthal*-p-*iodoanil*, bright yellow blades, decomposing without melting at about 381° (corr.); *tetrabromophthal*-3:4-*dimethylanil*, colourless plates, m. p. 264·5—271° (corr.); *tetrabromophthal*-2:4:5-*trimethylanil*, flat, colourless crystals, m. p. 307—308° (corr.); *tetrabromophthal*-o-*carboxyanil*, colourless prisms, m. p. 315·5—316·5° (corr.); *tetrabromophthal*-o-*ethoxyanil*, small, iridescent, light yellow plates, m. p. 247—248° (corr.); *tetrabromophthal*-p-*ethoxyanil*, light yellow crystals, m. p. 272·5—273° (corr.); *tetrabromophthal*-α-*naphthylimide*, light yellow needles, m. p. 309—309·5° (corr.); *tetrabromophthal*-β-*naphthylimide*, greenish-yellow plates, m. p. 305·5—308° (corr.); *tetrabromophthal*-p-*aminoazobenzene*, orange plates, m. p. 328·5—330° (corr.); *tetrabromophthalsemicarbazone*, short prisms with faint green tinge, which become red at 100°; *tetrabromophthalphenylhydrazone*, pale orange blades, m. p. 314—317·5° (corr.); *tetrabromophthalphenylethylhydrazone* separates from acetic acid in bright red needles, m. p. 211·0—211·5° (corr.), from benzene, ethyl acetate, or xylene in yellow needles, which become red at 95—96° and melt at the same temperature as the red variety. The crystals from benzene contain 1 mol. C_6H_6. The red variety becomes yellow when kept in a desiccator over benzene, and absorbs $\frac{2}{3}$ mol. C_6H_6; *tetrabromophthal*-2:4:6-*tribromophenylhydrazone* forms fine, hair-like needles, m. p. 290—291° (corr.); it appears to be unstable. H. W.

Phthalic Acid Derivatives: Constitution and Colour. 3:4:6-Tri-iodophthaloxime and its Derivatives. DAVID S PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1425—1428).—The compounds were prepared with the object of investigating possible cases of dimorphism, such as had been observed with tetrachlorophthaloxime (this vol., i, 171), but not with phthaloxime or tetraiodophthaloxime (*loc. cit.*, i, 172).

3:4:6-*Tri-iodophthaloxime* has been prepared from tri-iodophthalic anhydride; it exists in only one form, long, lemon-yellow needles, m. p. 224—226° (decomp.). The *ammonium*, *sodium*, *potassium*, and *silver* salts are described. The following ethers are conveniently prepared by treating an alcoholic suspension of the silver salt with the requisite alkyl haloid: *methyl ether*, canary-yellow blades and needles, decomposing without melting at 245—253°; *ethyl ether*, pale yellow masses of confused, curved needles, m. p. 241·5—242·5°; iso*propyl ether*, yellow needles, m. p. 182—186°; *allyl ether*, coarse, deep yellow prisms, m. p. 192—192·5°; *benzyl ether*, glistening, yellow plates, m. p. 217—217·5°. The *acetate* forms pale yellow, lenticular blades m. p. 223—224°; the *benzoate*, deep yellow, lenticular blades m. p. 224—225°. All the temperatures recorded are corrected. H. W.

The Nitration of 2- and 6-Methoxy-*m*-tolualdehydes and *m*-Toluic Acids. JOHN LIONEL SIMONSEN (T., 1918, **113** 775—782).—In the hope of preparing 3-methoxy-4-methylphthali

acid, the author has studied the nitration of 2-methoxy-*m*-tolualdehyde; the action, however, follows an unexpected course, and yields 5-*nitro-2-methoxy*-m-*tolualdehyde*, needles, m. p. 61—62° (*semicarbazone*, fine, woolly needles, decomposing at 233°); the constitution of the aldehyde follows from its oxidation to 5-*nitro-2-methoxy*-m-*toluic acid*, silky needles, m. p. 154°, which is also obtained by methylation of the corresponding hydroxy-acid (Einhorn and Pfyl, A., 1900, i, 439) and by nitration of 2-*methoxy*-m-*toluic acid*, hair-like needles, m. p. 83° (the *silver* salt forms a caseous, white precipitate).

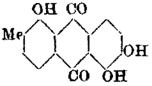
6-Methoxy-*m*-tolualdehyde is converted by nitric acid into 5-*nitro-6-methoxy*-m-*tolualdehyde*, needles, m. p. 77° (*semicarbazone*, needles, decomposing at 235°), which is readily oxidised to 5-*nitro-6-methoxy*-m-*toluic acid*, felted needles, m. p. 180—181° (the *barium*, *calcium*, and *silver* salts, and the *methyl* ester, needles m. p. 47°, are described). The same acid, together with a *substance*, probably 6-*nitro*-o-*tolyl methyl ether*, m. p. 69°, is obtained by nitration of 6-methoxy-*m*-toluic acid. The constitution of the ether is deduced from its oxidation to 6-*nitro-2-methoxybenzoic acid*, m. p. 161°, but the quantity of the latter which was available did not permit an extended investigation.

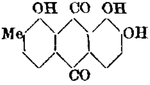
5 : 5′-*Dinitro-2 : 2′-dimethoxydi-3-methylstyryl ketone*, fine yellow needles, decomposing at 252°, and 5 : 5′-*dinitro-4 : 4′-dimethoxydi-3-methylstyryl ketone*, yellow needles, m. p. 214°, are prepared from the corresponding aldehydes. H. W.

Preparation of 1-Monohydroxy- and 1 : 8-Dihydroxy-anthranol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 305886; additional to D.R.-P. 296091; from *Chem. Zentr.*, 1918, ii, 238).—The alkyl ethers of 1-hydroxy- and 1 : 8-dihydroxy-anthraquinones are reduced by zinc in acid solution in the place of the parent substances (compare this vol., i, 111). The methyl ethers are cited as examples. H. W.

Morindone. JOHN LIONEL SIMONSEN (T., 1918, **113**, 766—774).—Although certain unexplained discrepancies exist between the results of Oesterle and Tisza (A., 1908, ii, 527) and Perkin and Hummel (T., 1894, **65**, 851), the author considers morindone obtained from *Morinda citrafolia* to be identical with that derived from *M. umbellata*.

Morindone is probably a hydroxymethylanthrarufin (I) or a hydroxymethylchrysazin (II) (annexed formulæ), for the following reasons. The methyl group is in position 2, since morindone can be converted into 2-methylanthracene (Perkin and Hummel, *loc. cit.*). Morindone contains three hydroxy-groups, since it yields triacetyl, tribenzoyl (yellow


(I.)


(II.)

needles, m. p. 218—219°), and trimethyl derivatives. Two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yields a monomethyl *ether*, brown needles, m. p. 248°. Further, morindone is a mordant dye resembling alizarin, and hence probably has two of the hydroxy-groups in the 1:2-position. The hydroxy-group, which undergoes methylation with methyl iodide, must be present in the same ring as another hydroxy-group, since morindone monomethyl ether is *completely destroyed on oxidation. Morindone cannot be a deriv*ative of anthragallol or purpurin, since it is perfectly stable in alkaline solution. Hence it follows that the only positions for the hydroxyl groups are as in 1:5:6- or 1:7:8-trihydroxyanthraquinone.

Further, it is highly probable that the methyl group is in the ortho-position with respect to one of the hydroxyl groups, since all attempts to oxidise it to a carboxyl group failed. Four formulæ are thus possible, of which the two quoted above are most probable, preference being given to (I), since morindone resembles more closely hydroxyanthrarufin than hydroxychrysazin in its colour reactions.

The presence of a $-CH_2 \cdot OH$ group in morindone, as suggested by Perkin (Thorpe's Dictionary, III. 547), is unlikely.

Attempts to isolate in a pure state the sugar obtained by the hydrolysis of morindin were unsuccessful. H. W.

Complete Synthesis of Norcamphor. S. V. HINTIKKA and GUST. KOMPPA (*Ann. Acad. Sci. Fennicae*, 1918, [*A*], **10**, No. 22, 1—12; from *Chem. Zentr.*, 1918, ii, 369—370).—Ethyl*cyclo*pentane-1-one-2-carboxylate is condensed by heating with zinc in benzene solution with methyl bromoacetate to *ethyl methyl hydroxyhomonorcamphorate* (annexed formula), a viscous, colourless oil, b. p. 140—172°/14 mm., which is converted by heating with sodium hydrogen sulphate at 120—140° into *methyl ethyl dehydrohomonorcamphorate*, $C_{11}H_{16}O_4$, a colourless oil, b. p. 143—145°/12 mm., D_4^{17} 1·09078, n_D 1·46956. On reduction with hydrogen and colloidal platinum, the latter yields *methyl ethyl homonorcamphorate*, b. p. 135—141°/13 mm., D_4^{17} 1·06829, n_D 1·45054. The corresponding *acid* separates from water in monoclinic prisms, from ether in radiating needles, and has m. p. 137—137·5° (corr.). The *lead* salt is crystalline; the *anilide* forms needles, m. p. 195—198·5°. *Norcamphor* is obtained in the form of readily volatile crystals, m. p. 93—94°, by dry distillation of the above-mentioned lead salt in an atmosphere of carbon dioxide; the *semicarbazone* has m. p. 196·5—197·5°.

$$\begin{array}{l} CH_2\cdot CH\cdot CO_2Et \\ \vert \qquad \vert \\ \vert \quad\; CH_2 \\ \vert \qquad \vert \\ CH_2\cdot C(OH)\cdot CH_2\cdot CO_2Me \end{array}$$

Attempts to prepare norcamphor from *cyclo*pentanedicarboxylic anhydride failed, on account of the difficulty of obtaining the latter in requisite quantity. In another series of experiments, lack

of success was due to inability to effect a normal hydrolysis or reduction of *ethyl cyanodehydrohomonorcamphorate*, $C_{13}H_{27}O_4N$, colourless oil, b. p. 189°/10 mm. (obtained by condensation of ethyl *cyclo*pentan-1-one-3-carboxylate with ethyl cyanoacetate in the presence of diethylamine), to homonorcamphoric acid.

H. W.

Conversion of Menthone into Pulegenone. O. WALLACH and E. GROTE (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 319—333; from *Chem. Zentr.*, 1918, ii, 120—121).—It has been shown previously (A., 1916, i, 487) that in the transformation of the dibromides of *cyclo*hexanones into *cyclo*pentanones, intermediate compounds of the general formula $C_nH_{2n-4}O_2$ are obtained which are regarded as hydroxy-ketones, and can be further converted into *cyclo*pentanehydroxycarboxylic acids and *cyclo*pentanones. In this manner, menthone yields two isomeric compounds, $C_{10}H_{16}O_2$ (α-compound, m. p. 82—83°, β-compound, m. p. 36—38°), of which the α-isomeride proves to be identical with buchu-camphor. These compounds have now been further investigated.

The two substances, $C_{10}H_{16}O_2$, appear to behave similarly towards bromine; a mixture of them is converted by this reagent in acetic acid solution into a monobromide, $C_{10}H_{15}O_2Br$, m. p. 77—78°, identical with the monobromobuchu-camphor described by Cusmano (A., 1914, i, 303). When warmed with anhydrous pyridine or sodium hydroxide solution, the monobromide yields hydroxythymoquinone. A second *monobromide*, $C_{10}H_{15}O_2Br$ (?), yellow crystals, m. p. 100—101°, or possibly somewhat higher (decomp.), is prepared by brominating in acetic acid solution at 60°. The *dibromide*, $C_{10}H_{14}O_2Br_2$, yellow crystals with green glance, m. p. 44—45°, is obtained by the action of an excess of bromine on an ethereal solution of the monobromide, m. p. 77°, or of buchu-camphor; it is not decomposed by boiling acetic acid, and is reduced by acetic acid and zinc dust to buchu-camphor; when warmed with pyridine, it yields a colourless oil, the alkaline solution of which is oxidised by air to hydroxythymoquinone. Aqueous potassium hydroxide transforms the dibromide into an *acid*, $C_{10}H_{18}O_5,H_2O$, transparent prisms, m. p. 88—89°, the *silver* salt of which is described. This acid, on dry distillation, yields pulegenone (methyl*iso*propyl-Δ^3-*cyclo*penten-2-one), b. p. 188·5—189°, n_D^{20} 1·4660 (semicarbazone, m. p. 183—184°). The ketone is reduced by hydrogen in the presence of palladium to dihydrocamphorphorone.

The previously described compound, $C_7H_{10}O_2$ (from the dibromide of methyl*cyclo*hexan-2-one, *loc. cit.*), is converted by excess of bromine in ethereal solution into a *tribromide*, $C_7H_7O_2Br_3$, yellow, hexagonal plates, m. p. 115—116°, which dissolves in alkali, yielding an acid containing bromine.

H. W.

New Synthetic Glucosides. FERDINAND MAUTHNER (*J. pr. Chem.*, 1918, [ii], **97**, 217—224. Compare A., 1912, i, 574; 1914, i, 195).—A solution of acetovanillone in aqueous sodium hydroxide

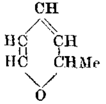
and acetone is treated below 18° with an acetone solution of acetobromoglucose, whereby *tetra-acetylglucoacetovanillone*, $C_{23}H_{28}O_{12}$, colourless crystals, m. p. 156—157°, is obtained, which yields by hydrolysis with 6% barium hydroxide solution *glucoacetovanillone*, $C_{15}H_{20}O_8$, colourless needles, m. p. 223—224°.

In a similar manner, the following glucosides have been prepared: *methyl tetra-acetylglucosalicylate* (*tetra-acetylgaultherin*), $C_{22}H_{26}O_{12}$, colourless leaflets, m. p. 154—155°, from methyl salicylate; *methyl tetra-acetylgluco-p-coumarate*, $C_{24}H_{28}O_{12}$, colourless crystals, m. p. 160—161°, from methyl *p*-coumarate (*gluco-p-coumaric acid*, $C_{15}H_{18}O_8$, forms colourless needles, m. p. 194—195°); *methyl tetra-acetylglucoferulate*, $C_{25}H_{30}O_{13}$, colourless needles, m. p. 125—126°, from methyl ferulate (*glucoferulic acid*, $C_{16}H_{20}O_9$, forms colourless needles, m. p. 186—187°). C. S.

Conversion of Mannitol into Methyl-α-pyran. A. Windaus and A. Tomich (*Nachr. K. Ges. Wiss. Gottingen*, 1917, 462—468; from *Chem. Zentr.*, 1918, ii, 109).—It has been shown by Fauconnier (A., 1885, 743) that mannitol is converted by formic acid into mannitan, $C_6H_{12}O_5$, and *iso*mannide, $C_6H_{10}O_4$; the former is esterified by formic acid, yielding a diformate which, at 210°, undergoes decomposition according to the schemes:

$$C_6H_{10}O_3(O\cdot COH)_2 = CO + CO_2 + C_6H_{12}O_4$$

and $C_6H_{10}O_3(O\cdot COH)_2 = 2H_2O + 2CO_2 + C_6H_8O$. The latter substance, C_6H_8O, has been obtained in a different manner by the authors. Closer investigation shows it to be methyl-α-pyran (annexed formula), since it passes into δ-hexylene oxide (compare Lipp, A., 1886, 219) when reduced by hydrogen in the presence of spongy palladium. The identity of products is further proved by converting each into the same dibromide, $C_6H_{12}Br_2$. H. W.



Derivatives of Berberine Closely Allied to Derivatives of Cryptopine. William Henry Perkin, jun. (T., 1918, **113**, 722—765).—The close relationship which exists between cryptopine and berberine has been previously discussed (T., 1916, **109**, 833, 841; 1918, **113**, 493); the object of the present investigation was to introduce an *N*-methyl group into the berberine molecule in order to study derivatives of berberine which are similarly constituted to the corresponding derivatives of cryptopine, and only differ from these in containing the two methoxy-groups and the methylenedioxy-group in the reversed positions.

The views of Gadamer (A., 1911, i, 152) with regard to the identity of dihydroanhydroberberine are substantially confirmed (compare Faltis, A., 1910, i, 698).

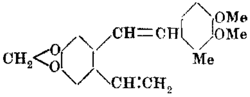
Dihydroanhydroberberine methosulphate, brilliant yellow, orthorhombic prisms, m. p. 205°, is converted into the *methochloride*, m. p. 223°, which, similarly to *iso*cryptopine chloride, is transformed into *anhydromethylberberine*, pale yellow prisms, m. p.

94—95°; the latter, on reduction, yields *N*-methyl*iso*tetrahydroanhydroberberine (Pyman, T., 1913, **103**, 827).

The behaviour of anhydromethylberberine and anhydrocryptopine with concentrated hydrochloric acid shows points of difference, but with the dilute acid the actions are very similar; thus, anhydromethylberberine gives two, probably stereoisomeric, *hydroxy*iso*anhydrodihydromethylberberines*, m. p.'s 210—212° and 168—170°, respectively. These are converted by acetyl chloride into mixtures of the *hydrochlorides* of two acetoxy*iso*anhydrodihydromethylberberines, from which the *acetyl* bases, m. p.'s 165—167° and 213—215°, respectively, are obtained.

iso*Anhydromethylberberine*, m. p. 123—124°, is prepared from either modification of hydroxy*iso*anhydrodihydromethylberberine; it yields a *hydrochloride*, m. p. 205—210°, and a *hydriodide*, m. p. 247°.

The reduction of dihydroanhydroberberine methochloride leads to the formation of the two modifications of the methochloride of tetrahydroanhydroberberine on the one hand, and of *dihydromethyl*iso*tetrahydroanhydroberberine* on the other (compare Pyman, T., 1913, **103**, 823); the methosulphate of the latter can be converted into *dihydrodimethyl*iso*tetrahydroanhydroberberine*. This substance similarly yields a methosulphate, from which *berberidene* (annexed formula), m. p. 113—114°, is derived. The main evidence in support of the formula is obtained by a study of the oxidation of the substance; it yields 5:6-dimethoxy-*o*-tolualdehyde, 5 : 6-dimethoxy-*o*-toluic acid, and an acid, m. p. 174—176°, which is doubtless hydrastic acid.



Anhydromethylberberine methosulphate, colourless needles, m. p. 150—152° (*methiodide*, m. p. 188—190°), resembles anhydrocryptopine methosulphate, in that it is converted by methyl-alcoholic potassium hydroxide into anhydromethylberberine; it is transformed by hydrochloric acid into *ψ-methylberberinium chloride*, m. p. 95—100° (*iodide*, m. p. 175—180°), which closely resembles ψ-cryptopine chloride.

Oxyberberine is readily reduced electrolytically to tetrahydroanhydroberberine, thus completing the synthesis of berberine devised by Pictet and Gams (A., 1911, i, 807).

For experimental details, the original must be consulted.

H. W.

Preparation of Hydrogenated Alkaloids. C. F. Boehringer & Söhne (D.R.-P. 306939; from *Chem. Zentr.*, 1918, ii, 421).—Alkaloids or their salts can be smoothly hydrogenated in aqueous solution or suspension by means of molecular hydrogen in the presence of nickel suboxide; the temperature may be normal or somewhat above (up to 60°), and the pressure normal or slightly

raised. Thus, hydroquinine and dihydromorphine are prepared from quinine hydrochloride and morphine, respectively, whilst cinnamylcocaine gives *hydrocinnamylcocaine*, an oily liquid which is decomposed by heat. H. W.

Pyrrole Blacks. A. ANGELI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 209—212; *Gazzetta*, 1918, **48**, ii, 21—25. Compare A., 1915, i, 9913).—As well as by the action of hydrogen peroxide in acetic acid solution, pyrrole is converted by most oxidising agents into highly coloured products, mostly black or brown, some being readily soluble and others insoluble in alkalis. Thus, addition of potassium dichromate to an acetic acid solution of pyrrole immediately precipitates an intensely black powder, and if a cotton fabric is soaked in the acid pyrrole solution and then transferred to the dichromate bath, it is dyed black, the colour being very fast against soap and light. This colouring matter contains chromium, probably combined, at least partly, with the colouring matter in the form of a lake. When treated with dilute sulphuric acid and dichromate, the black material passes into solution, and from the solution ether extracts maleimide, so that its molecule still contains pyrrole residues. It is probable that the series of changes: pyrrole ⟶ pyrrole black ⟶ maleimide is analogous to: aniline ⟶ aniline black ⟶ quinone.

The formation of pyrrole black seems to be preceded by polymerisation of the pyrrole molecule, this taking place with greater or less rapidity according to the reagents employed. The possible structures of these polymerides, their relation to the colouring matters, and the connexion of the latter with the black compounds formed as a result of the action of tyrosinase, are discussed.

T. H. P.

Pyrrole Blacks and Melanins. A. ANGELI (*Atti R. Accad. Lincei*, 1908, [v], **27**, i, 417—421).—In connexion with the close analogy between pyrrole blacks and natural melanins, as regards method of formation and also characters and behaviour (preceding abstract), the author directs attention to a number of cases of formation, either in the animal organism or through the agency of animal products, of dark pigments from pyrrole derivatives, and also from adrenaline, tyrosine, and hydroxyphenylethylamine, these compounds having skeletons similar to that of pyrrole.

T. H. P.

The Compounds of Phenol and the Cresols with Pyridine. II. F. W. SKIRROW and T. V. BINMORE (*J. Amer. Chem. Soc.*, 1918, **40**, 1431—1442. Compare Hatcher and Skirrow, A., 1917, i, 665). —The effect of excess of phenol and excess of pyridine on the dissociation of pyridine-phenol, postulated as $C_6H_5{\cdot}OH,C_5H_5N \rightleftharpoons C_6H_5{\cdot}OH + C_5H_5N$, has been studied by the cryoscopic method, and it has been found that phenol depresses the dissociation much more strongly than does pyridine. The dominant equilibrium might

therefore be $(C_6H_5{\cdot}OH)_2,C_5H_5N \rightleftharpoons 2C_6H_5{\cdot}OH + C_5H_5N$, but a study of this dissociation on similar lines showed that the effect of excess of phenol on the apparent dissociation was only greater than the effect of excess of pyridine with comparatively high additions of these. An explanation of these results and of the extraction results of the earlier paper is based on the following equilibria: $C_6H_5{\cdot}OH,C_5H_5N \rightleftharpoons C_6H_5{\cdot}OH + C_5H_5N$ and $C_6H_5{\cdot}OH,C_5H_5N + C_6H_5{\cdot}OH \rightleftharpoons (C_6H_5{\cdot}OH)_2,C_5H_5N$.

It is shown that the difference between the effect of addition of excess of phenol and of excess of pyridine in the extraction experiments tends to disappear as the dilution of the benzene solution is increased. H. W.

Preparation of Derivatives of Hydroxyarylquinolinedicarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 305885; additional to D.R.-P. 293467; from *Chem. Zentr.*, 1918, ii, 237).—Derivatives of isatic acid, substituted in the nucleus, are condensed with acetylsalicylic or acetylcresotic acids. Thus, *hydroxytolylquinolinedicarboxylic acid*, orange powder, decomposing above 280°, is prepared by warming 5-methylisatin with *p*-acetylsalicylic acid in the presence of potassium hydroxide and water. Similarly, 5:6-methylenedioxyisatin and *p*-acetylsalicylic acid yields a *quinolinedicarboxylic acid*, yellow powder. The product obtained from 5-methylisatin and acetyl-*p*-cresotic acid is a yellowish-red *powder* which decomposes at 290°. 6-*Bromo-4'-hydroxyphenylquinoline-4:3'-dicarboxylic acid*, yellow powder, decomposing at about 273°, results from 5-bromoisatin and *p*-acetylsalicylic acid. H. W.

N-**Acyl Derivatives of Carbazole.** MAURICE COPISAROW (T., 1918, **113**, 816—820).—Good yields of *N*-acylcarbazoles are obtained by triturating potassium carbazole with a slight excess of the requisite acid chloride; the energy of reaction and the stability of the products decrease with the complexity of the acyl group in the case of monobasic acids.

The action has been studied in the cases of acetyl, benzoyl, phenoxyacetyl, *n*-nonoyl, palmityl, carbonyl, and oxalyl chlorides.

It is improbable that *N*-oxalylcarbazole is an intermediate product in the formation of "carbazole-blue."

For experimental details, the original paper must be consulted. H. W.

Preparation of Piperazine. DAVID S. PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1428—1431. Compare D.R.-P. 60547).—The following process has proved satisfactory, but may be capable of improvement on a manufacturing scale. A mixture of ethylene bromide, aniline, and anhydrous sodium carbonate is heated to gentle boiling for five to six hours, the warm fused mass is extracted with hot water, and the crude diphenylpiperazine transformed into its nitroso-derivative by suspending it in cold concentrated hydrochloric acid and gradually adding a satu-

rated solution of sodium nitrite through a tube reaching to the bottom of the acid. The precipitate, probably the hydrochloride of dinitrosodiphenylpiperazine, is added to a 40% solution of sodium hydrogen sulphite and the suspension warmed to about 80°; the solution is made strongly alkaline with sodium hydroxide and concentrated by distillation. The piperazine is finally isolated by distillation of the residue with superheated steam and is absorbed by hydrochloric acid.

Traces of piperazine are conveniently detected by means of platinic chloride, picric acid, or bismuth potassium iodide (brilliant garnet crystals), or by the formation of dinitrosopiperazine.

H. W.

Formulation of so-called Quinonoid Dyes. HANS EDUARD FIERZ and HARTMANN KOECHLIN (*Helv. Chim. Acta*, 1918, **1**, 210—218).—The authors propose to apply, with certain modifications, Werner's views of the structure of inorganic compounds to quinonoid dyes, and to formulate these as complex compounds. Thus, rosaniline chloride is represented by the formula

$$[(NH_2\cdot C_6H_4)_3\vdots C]Cl,$$

and similar formulæ are given for dyes of the diphenylmethane, azine, thiazine, oxazine, and xanthene classes. The conversion of a coloured "ammonium" base into a colourless carbinol is represented by the formulæ $[(NH_2\cdot C_6H_4)_3\vdots C]OH \longrightarrow$

$$(NH_2\cdot C_6H_4)_3\vdots C\cdot OH,$$

the hydroxyl group being attached definitely to the carbon atom instead of indefinitely to the whole complex. The colour changes produced by mineral acids in aqueous solutions of triphenylmethane dyes find a simple explanation if the assumption is made that with increasing concentration of the acid molecules of the acid enter the complex and modify the auxochromic influence of the amino- or substituted amino-groups.

C. S.

Explanation of Heumann's Rosaniline Synthesis. HANS EDUARD FIERZ and HARTMANN KOECHLIN (*Helv. Chim. Acta*, 1918, **1**, 218—226).—In the original Heumann reaction (D.R.-P. 66511 and 68976), carbon tetrachloride and a tertiary amine, for example, dimethylaniline, are made to react in the presence of aluminium chloride, whereby crystal-violet or an analogous product is at once obtained. The authors state that the primary product is the keto-chloride, $CCl_2(C_6H_4\cdot NMe_2)_2$ (although they have not succeeded in isolating it), because the reaction product, after heating at 50° has been continued for ten minutes, yields a small quantity of Michler's ketone when added to ice-water. When acetanilide is used instead of dimethylaniline, and the temperature not allowed to exceed 30° during the reaction, a 60% yield of 4:4′-diaminobenzophenone is obtained on adding the reaction product to ice-water and hydrolysing the product with dilute sulphuric acid (1:1) at 110—115°.

4:4′-Diaminobenzophenone, which thus becomes an easily obtainable substance, forms a *diacetyl* derivative, colourless needles,

m. p. 237°, a *dibenzylidene* derivative, colourless needles, m. p. 194°, and a *phenylhydrazone*, faintly rose-coloured needles, m. p. 240°. 3 : 3'-*Dichloro*-4 : 4'-*diaminobenzophenone*, a yellow, crystalline powder, is obtained from *o*-chloroacetanilide, and 4 : 4'-tetramethyldiamino-2 : 2'-dimethylbenzophenone from dimethyl-*m*-toluidine in a similar manner.

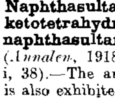
Tetrazotised diaminobenzophenone couples with β-naphthol and with naphthol A.S. to produce bisazo-dyes of little interest.

The keto-chloride obtained from acetanilide reacts with dimethylaniline to produce 4-*dimethylamino*-4' : 4''-*diacetylaminotriphenylmethyl chloride*, $NMe_2\cdot C_6H_4\cdot CCl(C_6H_4\cdot NHAc)_2$, which dyes silk and wool grey; after hydrolysis of the acetyl groups, the resulting base dyes silk and wool violet.

The keto-chloride obtained from dimethyl-*m*-toluidine reacts with a further quantity of the same base to produce hexamethyltriaminotri-*m*-tolylmethyl chloride, which dyes silk and wool in pure blue tones. C. S.

Naphthasultam. III. Nitro- and Amino-derivatives of Naphthasultam, and Hydrolytic Products of Tetrachloroketotetrahydronaphthasultam [2 : 2 : 3 : 3-Tetrachloro-1 : 8-naphthasultam-4-quinone]. TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1918, **416**, 65—85. Compare A., 1916, i, 426; 1917, i, 38).—The analogy between 1 : 8-naphthasultam and α-naphthol is also exhibited by their nitro- and amino-derivatives.

When 1 : 8-naphthasultam is ground with nitric acid (D 1·2; 10 parts), it yields 2 : 4-*dinitro*-1 : 8-*naphthasultam*, $C_{10}H_5O_6N_3S$, in brownish-yellow tablets and prisms, m. p. 258° (decomp.), and forms deep yellow, crystalline ammonium, potassium, and sodium salts. Dannerth (A., 1907, i, 909) regarded the product as a mononitro-derivative. On reduction with tin and hydrochloric acid, the compound gives 2 : 4-*diamino*-1 : 8-*naphthasultam*; this crystallises in slender, yellow needles, which soon become dark on exposure to the air, and forms a *monohydrochloride*, yellow needles, a *dihydrochloride*, pale yellow needles, and a *triacetyl* derivative, white needles, m. p. above 270°, which changes into 2 : 4-*diacetylamino*-1 : 8-*naphthasultam*, $C_{14}H_{13}O_4N_3S$, when shaken with dilute alkali hydroxide (compare Dannerth, *ibid.*). The hydrochlorides are oxidised by ferric chloride to 2-*amino*-1 : 8-*naphthasultam*-4-*quinoneimide* (annexed formula), a reddish-brown powder, which blackens at 230—235°, and forms a *hydrochloride*, dark red needles. The imide reacts with aniline in hot alcoholic acetic acid to give 2-*anilino*-1 : 8-*naphthasultam-quinoneanil*, $C_{22}H_{15}O_2N_3S$, which crystallises in bronzy-red needles, m. p. 235—236° and forms an almost black hydrochloride and nitrate.

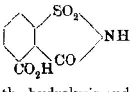


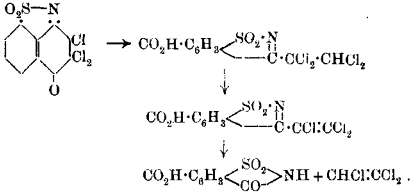
2 : 2 : 3 : 3-Tetrachloronaphthaquinone and 2 : 2 : 3 : 3-tetrachloro-1 : 8-naphthasultam-4-quinone resemble each other in their behaviour towards alkalis. If the latter is triturated for a few

minutes with aqueous-alcoholic sodium hydroxide, it is hydrolysed to *2-trichloroacrylyl-3-sulphamidobenzoic acid*,

$$CCl_2:CCl\cdot CO\cdot C_6H_3(CO_2H)\cdot SO_2\cdot NH_2,$$

which crystallises in stout tablets from dilute alcohol or long needles from dilute hydrochloric acid, has m. p. 197—198° (decomp.), and forms a *methyl* ester, stout prisms and tablets, m. p. 115—116°. Both the acid and the ester deposit trichloroethylene on shaking with alkali hydroxide, the solution containing the salt of *phthalicsulphinide* ("*saccharincarboxylic acid*") (annexed formula). This acid may be obtained directly from the quinone by prolonging the action of alkali to two hours, the hydrolysis and subsequent reactions being represented as follows:





Phthalicsulphinide crystallises in stout, hard needles, m. p. 275—276°, and whilst it is stable towards dilute alkalis, it is readily hydrolysed by boiling with dilute hydrochloric acid to *3-sulphamidophthalic acid*, $NH_2\cdot SO_2\cdot C_6H_3(CO_2H)_2$, which crystallises with $1H_2O$ in glistening leaflets or broad needles, m. p. 165° (decomp.), the anhydrous acid having m. p. 194°, and changing at this temperature, or when warmed with concentrated sulphuric acid, into phthalicsulphinide. The acid is stable towards boiling *N*-alkali hydroxide, but its *methyl* ester, glistening leaflets, m. p. 139°, changes into phthalicsulphinide when shaken with alkali hydroxide in the cold. Conversely, phthalicsulphinide yields this methyl ester when warmed with methyl-alcoholic hydrogen chloride. These derivatives of phthalic acid were originally described by Comstock (1883), Stokes (1884), and Moulton (1891), working under Remsen's guidance, but they failed to differentiate clearly between phthalicsulphinide and sulphamidophthalic acid.

J. C. W.

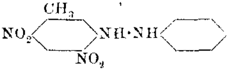
Analogies in Behaviour between the Diazoimide and Diazomethane Rings. E. Oliveri-Mandalà (*Gazzetta*, 1918, **48**, ii, 35—39).—A very brief summary of the principal results of a number of papers published in the years 1910—1915. T. H. P.

Electrolytic Reduction of Hydroxyazo-compounds. E. Puxeddu (*Gazzetta*, 1918, **48**, ii, 25—30).—In alcoholic solution

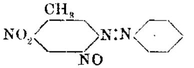
and in presence of hydrochloric acid, *p*-hydroxyazobenzene undergoes electrolytic reduction to *p*-aminophenol, whereas in presence of sulphuric and acetic acids no definite result is obtained.

T. H. P.

Aromatic Nitro-derivatives. VII. Formation of Nitrohydrazo-compounds. MICHELE GIUA (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 247—252; *Gazzetta*, 1918, **48**, ii, 8—17).—By the action of phenylhydrazine on trinitrotolylmethylnitroamine and on trinitromethyl-*p*-toluidine, Sommer (A., 1903, i, 655) obtained derivatives of hydrazobenzene. With aromatic polynitro-compounds containing a labile nitro-group, phenylhydrazine in the cold exerts not a reducing, but rather a substituting action. The author finds that this behaviour of phenylhydrazine is general in character, and furnishes a good method for preparing nitrohydrazo-compounds.



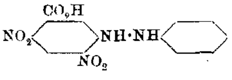
2 : 4-*Dinitro-5-methylhydrazobenzene* (annexed formula), obtained by the action of phenylhydrazine on 2 : 4 : 5-trinitrotoluene in methyl-alcoholic solution, forms reddish-yellow plates, m. p. 155° (decomp.). When treated in alcoholic solution with gaseous hydrogen chloride, it is converted into 4-*nitro*-2-*nitroso*-5-*methylazobenzene* (annexed formula), which crystallises in golden-yellow plates, m. p. 120—121°.

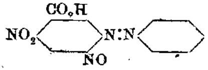


2 : 6-*Dinitro-5-methylhydrazobenzene*, $C_{13}H_{12}O_4N_4$, obtained from phenylhydrazine and 2 : 3 : 4-trinitrotoluene, forms large, red prisms, m. p. 137° (decomp.), and by gaseous hydrogen chloride in alcoholic solution is converted into 6-*nitro*-2-*nitroso*-5-*methylazobenzene* or 2-*nitro*-6-*nitroso*-5-*methylazobenzene*, $C_{13}H_{10}O_3N_4$, which crystallises in shining, yellow needles, m. p. 154°.

T. H. P.

Aromatic Nitro-derivatives. Formation of Nitrohydrazo-compounds. MICHELE GIUA (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 379—382. Compare preceding abstract).—2′ : 4′-*Dinitrobenzeneazo*-m-*benzoic acid* (annexed formula), prepared, together with a brown compound, m. p. below 100°, by the action of phenylhydrazine on 2 : 4 : 5-trinitrobenzoic acid, forms yellow needles, m. p. 135° decomp.); its *silver* salt was analysed. When dissolved in methyl alcohol and treated with gaseous hydrogen chloride, it yields 4′-*nitro*-2′-*nitrosobenzene*-m-*azobenzoic acid* (annexed formula), which crystallises in golden-yellow needles, m. p. 244° (decomp.).





Methyl 2′ : 4′-*dinitrobenzenehydrazobenzoate*, $C_{14}H_{12}O_6N_4$, obtained from phenylhydrazine and methyl

2:4:5-trinitrobenzoate, forms shining, orange-red plates, m. p. 177—178° (decomp.); from methyl alcohol containing benzene, it crystallises along with an *isomeride*, which forms pale yellow, prismatic crystals, m. p. 147°; these begin to emit gas at 175—178°.

In the action of *as*-phenylmethylhydrazine on 2:4:5-trinitrotoluene, a similar substitution takes place, with elimination of nitrous acid and subsequent formation of nitrogen. T. H. P.

Hydrazino-acids. II. AUGUST DARAPSKY (*J. pr. Chem.*, 1918, [ii], **97**, 182—217. Compare *ibid.*, 1917, [ii], **96**, 251).—In addition to the five methods of preparing hydrazino-acids already described (*loc. cit.*), the author has examined the behaviour of mandelonitrile with hydrazine hydrate, and found that the reaction does not follow the expected course. A violent reaction ensues when the mixture is warmed on the water-bath, ammonia and hydrogen cyanide are evolved, and the dark red liquid deposits a small quantity of a substance, pale yellow leaflets, m. p. about 175°, which is not individual and probably contains diphenyldihydrotetrazine, since it yields diphenyltetrazine by oxidation. When the reaction proceeds in cold alcoholic solution, dibenzenylhydrazidine (Pinner, A., 1898, i, 94) is obtained; no trace of Purgotti's α-toluonitrile (A., 1895, i, 602) could be detected.

The behaviour of benzaldehyde towards hydrazine monohydrochloride and potassium cyanide is exactly analogous to that of formaldehyde (Jay and Curtius, A., 1894, i, 162). When equal molecular quantities of the three substances react in cold aqueous methyl-alcoholic solution, *α-benzylidenehydrazinophenylacetonitrile*, CHPh:N·NH·CHPh·CN, yellow leaflets, m. p. 112°, is obtained. If two molecules of benzaldehyde are used, or if hydrazine dihydrochloride is employed instead of the monohydrochloride, the product is benzylideneazine, a small amount of a by-product, colourless needles, m. p. 215°, being obtained in both cases. The α-benzylidenehydrazinophenylacetonitrile is probably formed from benzylidenehydrazine and mandelonitrile, the initial products of the reaction, since it is shown that these two substances react to produce the first under the experimental conditions. α-Benzylidenehydrazinophenylacetonitrile yields hydrogen cyanide, benzaldehyde, and hydrazine by hydrolysis with hot 20% hydrochloric acid, and *α-benzylidenehydrazinophenylacetamide*, colourless crystals, m. p. 165—167° (decomp.), by treatment with concentrated hydrochloric acid at the ordinary temperature. When the amide is treated with *N*-hydrochloric acid and an equal volume of water, and the mixture is distilled with steam, *α-hydrazinophenylacetamide hydrochloride*, NH_2·CO·CHPh·NH·NH_2,HCl, colourless leaflets, m. p. 215° (decomp.), is obtained, which can be converted into *α-benzylidenehydrazinophenylacetic acid*, $C_{15}H_{14}O_2N_2$, long needles, m. p. 150°, and into *α-hydrazinophenylacetic acid*, colourless leaflets, m. p. 188—189°.

The preceding reaction between benzaldehyde, hydrazine monohydrochloride, and potassium cyanide is not a general one for

aromatic aldehydes, salicylaldehyde and anisaldehyde yielding only the respective aldazines. Heptaldehyde yields *heptylidenehydrazine*, $C_6H_{13}\cdot CH:N\cdot NH_2$, colourless leaflets, m. p. 133—136°, which is also obtained from aqueous hydrazine hydrate and heptaldehyde, the substance described under this name by Franzen and Eichler (A., 1910, i, 700) being really heptylideneazine.

By heating a mixture of equal molecular quantities of benzylidenehydrazine and heptaldehyde cyanohydrin on the water-bath, an oil is obtained which has the composition of benzylideneheptylideneazine, but it is probably not an individual substance, since it slowly deposits yellow crystals of benzaldazine. C. S.

Relative Masses of Protein Anions and Cations. A. R. C. HAAS (*J. Physical Chem.*, 1918, **22**, 520—524).—A repetition of the work of Robertson on the transport of casein ions by an electric current (A., 1909, i, 619; 1910, i, 526). The change in the casein concentration at the anode and cathode in the electrolysis of potassium caseinate has been determined by Robertson's method and by determination of the change in the nitrogen content at both electrodes. The results confirm those of Robertson, which show that the ratio of the loss at the anode to that at the cathode is 2. This proves that the masses of the protein anions and cations are equal, and that the current is carried in both directions by protein ions. J. F. S.

Mucins and Mucoids. P. A. LEVENE and J. LÓPEZ-SUÁREZ (*J. Biol. Chem.*, 1918, **36**, 105—126. Compare A., 1916, i, 681, 765).—Mucoids containing chondroitin–sulphuric acid have been obtained from the aorta and the sclera. On hydrolysis, chitosamine is produced.

Mucoitin–sulphuric acid has been obtained from funis mucin, vitreous humour, cornea, mucin of gastric mucosa, serum mucoid, ovomucoid, and ovarian cysts. On hydrolysis with hydrochloric acid, mucoitin–sulphuric acid yields *mucosin*, $C_{12}H_{21}O_{11}N,HCl$, white powder, $[\alpha]_D^{20}$ +25·55°, which is a disaccharide composed of glycuronic acid and chitosamine. H. W. B.

Behaviour of Thymic Acid to Phenylhydrazine. R. FEULGEN and G. LANDMANN (*Zeitsch. physiol. Chem.*, 1918, **102**, 262—265. Compare Feulgen, this vol., i, 85, 413).—Further evidence of the existence of two free aldehydic groups in thymic acid is furnished by the preparation of a diphenylhydrazone of the acid, which is isolated in the form of its barium salt. Barium thymate is dissolved in water and treated at 60° with phenylhydrazine in acetic acid solution. The temperature is then raised to 100°, and the heating continued for twenty minutes. Barium acetate is now added, and then three volumes of boiling alcohol. After cooling, the precipitated phenylhydrazone is purified by reprecipitation by alcohol from its solution in dilute acetic acid. *Barium phenylhydrazinothymate*, $C_{45}H_{53}O_{24}N_9P_4Ba_2$, is a yellow,

amorphous substance which readily decomposes when heated or treated with strong acids. Crystalline derivatives have not been obtained. H. W. B.

Influence of certain Salts on Enzyme Action. I. S. FALK (*J. Biol. Chem.*, 1918, **36**, 229—247).—Sodium chloride accelerates slightly the rate of lipolysis of olive oil by lipase, whilst calcium chloride always inhibits it. The former does not alter the point of equilibrium of the reaction mixture; when calcium chloride is present, equilibrium is reached very much earlier than in its absence, and the higher the concentration, the greater the influence on the lipase. The addition of sodium chloride tends to prevent the appearance of the calcium effect. H. W. B.

Peroxydases. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1918, **416**, 21—64).—The authors have set themselves the task of so improving the methods for isolating and purifying enzymes that the following questions may be answered: (1) whether enzymic activity is possessed by an analytically pure compound or whether an "enzyme" is a system of co-operating substances, (2) whether a metal is an integral part of an enzyme, and, eventually, (3) what atomic groupings are associated with enzyme activity. As a preliminary study, the case of horse-radish peroxydase has been chosen.

For the isolation of highly concentrated peroxydase preparations, the following scheme is recommended: (I) Thin slices of the roots (5 kilos.) are kept for a few days in flowing water in order to remove the simpler products by dialysis through the cell walls. (II) The washed material is then digested with oxalic acid solution (40 grams to 10 litres) for a few hours. By this means, the regulating influence of the living protoplasm is removed, the peroxydase is precipitated, apparently adsorbed on coagulated protein material, and dialysis proceeds further, mustard oil being extracted in large quantities. So extensive is the dialysis, that the dried slices lose more than 25% in weight and half of their mineral matter. (III) The material is next crushed in a mill, washed on a filter with about 15 litres of water containing 1·5 grams of oxalic acid, and then thoroughly pressed free from sap. The residue (1·5 kilos.) is intimately triturated with baryta water, almost sufficient to overcome its acidity, then pressed again, and now treated with further quantities of baryta water to liberate the enzyme. Most of the barium is retained by the fibres, but the expressed liquid is just acidified by means of carbon dioxide to remove the remainder, and then the filtrate is mixed with nine-tenths of its volume of alcohol. Slimy substances are precipitated, and the filtrate is evaporated to 50—70 c.c. in a vacuum, from a bath at 50°. The residue is filtered again and then mixed with five times its bulk of alcohol, whereby the crude enzyme is precipitated. This is purified a little more by redissolving it in water containing a trace of sulphuric acid and reprecipitating it by

alcohol. (IV) The crude material is found to be a mixture of the enzyme with a nitrogenous glucoside, which can be precipitated as a compound with mercuric chloride. Accordingly, an aqueous solution is treated with 0·5% mercuric chloride and a trace of *calcium chloride to coagulate the jelly-like double compound, the* mass is filtered, and the enzyme reprecipitated by alcohol from the filtrate. The peroxydase is then dissolved in water, whereby some of the mercuric chloride compound remains undissolved, the clear solution obtained by centrifuging is reprecipitated by alcohol, and the process repeated until the enzyme dissolves clearly in water. The best preparation obtained so far amounted to 0·45 gram from 5 kilos. of horse-radish, this representing about 60% of the enzyme originally present. The glucoside compound is decomposed by $2N$-hydrochloric acid, and the glucoside obtained by precipitating the solution with alcohol amounts to about 3·4 grams.

In order to control the above operations, a method for estimating peroxydase was developed. It depends on the production of purpurogallin from pyrogallol and hydrogen peroxide, but is free from certain errors which are present in Bach and Chodat's method (A., 1904, i, 542). It is found, namely, that peroxydase is not only spoilt by too great a concentration of hydrogen ions, but by too concentrated hydrogen peroxide, and it is only fair, therefore, in devising an analytical method, to choose conditions under which the enzyme is not impaired. The method proposed is as follows. A solution of 5 grams of purest pyrogallol in 2 litres of water is mixed with about 10 c.c. of 5% hydrogen peroxide containing exactly 50 mg. of H_2O_2, regulated to 20° in a thermostat, and then treated with 1—5 c.c. of a solution of 5 mg. of the enzyme in 100—500 c.c. of water (that is, from about 0·25 mg. of the crude preparations to 0·02 mg. of the best preparation). After exactly five minutes, the action is stopped by adding 50 c.c. of dilute sulphuric acid, the purpurogallin is extracted with ether and estimated colorimetrically by comparison with a solution containing 100 mg. of the pure pigment in 1 litre of ether. The results are then translated into the number of mg. of purpurogallin which would be produced by 1 mg. of the vacuum-dried preparation. This is called the "purpurogallin number." For example, the number for the well-pounded horse-radish is about 0·25, for the crude preparation before treatment with mercuric chloride about 360, and for the best specimen yet obtained about 670. In a solution of carbon dioxide, the enzyme is not impaired, but produces only about half as much purpurogallin as in pure water. It appears as though the particular grouping in the enzyme at which hydrogen peroxide may be attached is also capable of uniting with acids. Solutions of the preparations which have not been purified by mercuric chloride become somewhat more active after a few hours, but the solutions of the purified enzyme deteriorate. Consequently, any comparisons of activity are made immediately after dissolving the preparations.

The yield of purpurogallin obtainable from pyrogallol has often

been discussed. For example, *Nierenstein and Spiers* (A., 1913, i, 1367) obtained 10—16%. If the pyrogallol solution is concentrated, the amount of peroxydase employed is large, and the hydrogen peroxide is added very slowly, so that it is always present in very low concentrations, the yield may be as high as 80%.

Some reactions and analytical data concerning the purest enzyme and its companion glucoside are also recorded. The enzyme appears to consist chiefly of a nitrogenous glucoside, containing a pentose (above 30%) and an equimolecular quantity of another sugar, probably a hexose. It does not seem to be very complex, and if it contains only the residues of two sugar molecules, its molecular weight would be about 500 and number of nitrogen atoms 3. It also contains about 5·5% of mineral ash, consisting of alkaline earths and iron. The amount of the latter is very small (0·46% in the best preparation), but it rises with the purification of the enzyme. It is unlikely, however, that iron plays any stoicheiometrical part in the production of purpurogallin, for it may be calculated that the activity of the best preparation would mean a consumption of 297—355 molecules of hydrogen peroxide in one second for every atom of iron present. Furthermore, the addition of ferrous salts is of no influence in the reaction. The companion nitrogenous glucoside, which is precipitated by mercuric chloride, is a high molecular compound. Its vapours give the pyrrole reaction, and it also gives the Millon and xanthoproteic reactions. It contains about 50% of pentose residues, and a hexose, and the proportion of nitrogen is about 3 atoms to every 2 pentose molecules.

Oxyhæmoglobin has often been compared with peroxydase, and Wolff and de Stoecklin have even stated that they do not differ in peroxidative action (A., 1910, i, 802). This is chiefly because rich peroxydase preparations had not been employed hitherto, for oxyhæmoglobin is only about one-thousandth part as active as a quantity of peroxydase containing the same amount of iron. Iron compounds, such as the tannate or a ferrocyanide (Wolff, A., 1911, ii, 795) or sulphate, are also very feeble in their activity compared with peroxydase. J. C. W.

Physiological Chemistry.

Distribution of Phosphoric Acid in Normal Human Blood. W. R. Bloor (*J. Biol. Chem.*, 1918, **36**, 49—57).—There are two classes of phosphoric acid compounds in human blood, (1) those soluble in dilute acids and precipitated by alcohol-ether, (2) those soluble in alcohol-ether and precipitated by dilute acids. The sum of these two groups is, in general, equal to the total phosphates, so that the presence of other forms of combina-

tion of the phosphoric acid in blood, in significant amounts, is improbable.

The second group contains substances of the type of lecithin; the first group comprises the inorganic phosphates and an unknown compound, which is decomposed by heating with acids, yielding phosphoric acid. The amount of the unknown compound in plasma is about 10% of the total phosphates, whilst in the corpuscles it ranges between 60% to 80% of the total phosphates. The possible significance of this compound is discussed. H. W. B.

Phenols and Phenol Derivatives in Human Blood in some Pathological Conditions. RUTH C. THEIS and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **36**, 99—103).—By means of the method previously described (this vol., ii, 461), it is found that the amount of phenols in pathological blood may vary between 1·87 and 7·96 mg. per 100 c.c. of blood. H. W. B.

The Pigments of Blood Serum. G. PATEIN (*J. Pharm. Chim.*, 1918, [vii], **18**, 225—238).—From a series of tests, the author concludes that Fouchet's method (compare this vol., ii, 415) for the detection of biliary pigments in serum is not vitiated by the presence of indoxyl. The methods of Troisier and Berthelot (compare *Compt. rend. Soc. Biol.*, 1912, 259) and of Giraud and Montpellier (compare *Bull. Soc. chim.*, 1917, 132) for the detection of indoxyl give good results. If the amount of indoxyl present is small, it is better to extract it from the serum with alcohol and examine the residue left after evaporating the alcohol. The addition of a trace of ferric chloride to the hydrochloric acid makes the reaction more sensitive.

A new blue pigment has been discovered in blood serum which does not form under the oxidising action of reagents. It is characterised by its solubility in 0·6% sodium chloride solution and its insolubility in the solvents which dissolve the other pigments. It is much less stable than either bilicyanin or indigotin. At present it is only possible to state that it is a complex formed by a blue substance and globulin. It has been found in most of the serums examined, but in very small amounts. W. G.

Concentration of Antitoxic Sera by the Salting Out of the Heat-denaturated Serum Proteins with Sodium Chloride. ANNIE HOMER (*Biochem. J.*, 1918, **12**, 190—209).—The concentration of antitoxic sera can be successfully conducted by a regulation of the heat-denaturation of the serum proteins, followed by a direct treatment of the heated sera with brine and salt. The end-products thus obtained are clear and readily filterable, as they do not contain the colloidal suspension of heat-denaturated protein which is so often found in those resulting from methods involving the use of ammonium sulphate. The new method does not effect the removal of as great a proportion of the serum proteins as the Banzhaf and Homer methods (this vol.,

i, 138), and the degree of concentration of antitoxin in the end-product is also lower than can be obtained by the former methods.

H. W. B.

Uric Acid Metabolism. I. The Influence of High Protein Diets on the Elimination of Endogenous Uric Acid. HOWARD B. LEWIS and EDWARD A. DOISY (*J. Biol. Chem.*, 1918, **36**, 1—7).—No difference is observed in the amount of uric acid excreted by two men maintained for successive periods on purine-free high protein diets containing (*a*) much arginine and histidine, and (*b*) little of these amino-acids. This result does not appear to be in harmony with the conclusions drawn by Ackroyd and Hopkins (A., 1917, i, 237) from their experiments, namely, that arginine and histidine constitute the raw material for the synthesis of the purine ring in the animal body. H. W. B.

Uric Acid Metabolism. II. Proteins and Amino-acids as Factors in the Stimulation of Endogenous Uric Acid Metabolism. HOWARD B. LEWIS, MAX S. DUNN, and EDWARD A. DOISY (*J. Biol. Chem.*, 1918, **36**, 9—26. Compare this vol., i, 277).—A full account of work previously published.

H. W. B.

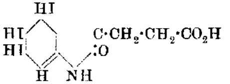
Rôle of Inorganic Sulphates in Nutrition. AMY L. DANIELS and JEAN K. RICH (*J. Biol. Chem.*, 1918, **36**, 27—32).—The addition of inorganic sulphates to the diet of young rats does not increase the rate of growth, even when the diet is deficient in cystine. These animals are apparently unable to synthesise cystine from inorganic sulphates. H. W. B.

Biochemical Mechanism of Growth. The Effect of Sodium and Calcium Ions on the Growth of a Transplantable Mouse Carcinoma. WILLIAM CRAMER (*Biochem. J.*, 1918, **12**, 210—220).—When the cells of a transplantable mouse carcinoma are placed in an isosmotic solution of calcium chloride, they lose water, and on subsequent transplantation show a much slower rate of growth than is exhibited by similar cells transplanted without any such treatment. Both the inhibition of growth and the loss of water produced by calcium ions can be antagonised by a subsequent suspension of the cells in sodium chloride solution. This inhibition of growth produced experimentally, and the subsequent recovery from it, present a similarity to the spontaneous fluctuations in growth which are exhibited normally by tumour cells in the course of their propagation. The bearing of these results on the question of the possibility of the discovery of a cure for cancer is discussed. H. W. B.

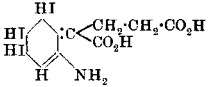
Rôle of the Liver in Hippuric Acid Synthesis. E. LACKNER, A. LEVINSON, and WITHROW MORSE (*Biochem. J.*, 1918, **12**, 184—189).—The injection into dogs of hydrazine sulphate,

which poisons the liver without interfering with the functions of the kidney, appears to inhibit the subsequent formation of hippuric acid from administered sodium benzoate. In dogs, therefore, as in rabbits, the liver seems to participate in the synthesis of hippuric acid (compare Kingsbury and Bell, A., 1915, i, 739). H. W. B.

Thyroid Hormone and its Relation to the other Ductless Glands. E. C. KENDALL (*Endocrinology*, 1918, **2**, 81—93. Compare A., 1917, i, 364).—The name *thyroxin* (from thyro-oxy-indole) is suggested for the active principle of the thyroid gland. It has the constitution I. In the alkaline body fluids it



(I.)



(II.)

is considered to occur in the hydrated condition (II). An adult has a total amount of 23—50 mg. A dose of $\frac{1}{3}$ mg. increases the basal metabolic rate by 1%, or a dose of 10 mg. by 30%. The synthesis of a small quautity is stated to have been effected by the author's collaborator, Osterberg. G. B.

Arginase. V. Presence of Arginase in the Organism of certain Invertebrates. A. CLEMENTI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 299—302).—The author's previous results render it of interest to ascertain if arginase exists in the organism of invertebrates, and if in the latter any relation is detectable between arginase and the type of the nitrogenous exchange. The work now described shows that this enzyme is absent from the aqueous extracts of the hepato-pancreas of *Astacus fluviatilis* and of the larvæ of thermites, but that it is present in the hepato-pancreas of *Helix pomatia*. T. H. P.

Hydrolysis of the Cocoon-silk of the Bivoltine Species "Daiwanishiki" (the Authum Breed), and of Sericine separated from the same Silk. RYŪGO INOYE and KATSU HIRASAWA (*J. Tokyo Chem. Soc.*, 1918, **39**, 300—320).—Cocoon silk, cultivated in the Ueda College of Sericulture in middle Japan, was hydrolysed, and the following percentages of amino-acids, calculated on the dry silk, were obtained by the ester method: glycine 25·42, alanine 22·58, leucine 0·62, aspartic acid 0·11, glutamic acid trace, proline 0·32, serine 2·77, phenylalanine 0·25, and tyrosine 5·68. The cocoon silk contained 24·2% of sericine, and this on hydrolysis yielded: glycine 3·86%, alanine 3·47%, leucine 0·39%, aspartic acid 3·91%, glutamic acid 0·81%, proline 0·35%, serine 5·89%, phenylalanine 0·49%, and tyrosine 3·18%.

The author draws the conclusion that the amino-acids contained in the silk of the bivoltine species seem to be quite similar in

amount and nature to those of the monovoltine species, but the sericine separated from the silk of the bivoltine species has a chemical constitution somewhat different from that of the monovoltine species, which have been investigated previously; that there is a difference is in agreement with the fact that the cocoons of the former species can be more easily reeled than those of the latter.

S. H.

Cholesterol in Milk. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1918, **36**, 59—61).—Cow's milk contains from 10 to 18 mg. of cholesterol per 100 c.c. of milk. The corresponding figures for human milk range between 10 and 40. The amount of cholesterol in the milk appears to be determined by the amount in the food.

H. W. B.

Detection, Estimation, and Elimination of Arsenic and Mercury in Urine. PAUL DURET (*Compt. rend. Soc. Biol.*, 1918, **81**, 736—737, 737—739).—In both cases, organic matter is destroyed by ammonium persulphate in sulphuric acid solution (compare this vol., ii, 335). Arsenic is estimated by converting it into arsenic trihydride and passing into silver nitrate; the reduced silver is estimated with potassium cyanide. Mercury is precipitated with ammonia, converted into the hydrochloride, and tested qualitatively in ethereal solution with diphenylcarbazide (blue coloration), and estimated with standard solutions of potassium cyanide and silver nitrate. After "novarsenobenzol" (neo-salvarsan), arsenic appears in the urine in the first twenty-four hours, and may persist for twenty days. The greatest amount eliminated was 12 mg. of arsenic in twenty-four hours after a dose of 900 mg. novarsenobenzol containing 190 mg. of metallic arsenic. The elimination is most rapid in the first forty-eight hours, and generally falls after four days to 1 mg. per twenty-four hours. Ten mg. per twenty-four hours is about the maximum with which the kidneys can deal. In a course of four injections at intervals of a week, scarcely one-fifth of the arsenic is eliminated.

Mercury appears in the urine in small quantities in the first twenty-four hours after injection. G. B.

Creatine Excretion in Ruminants. JOHN BOYD ORR (*Biochem. J.*, 1918, **12**, 221—230).—The amount of creatine excreted by a goat or a sheep is relatively large, and is inversely proportional to the amount of carbohydrate in the diet. Cessation of lactation causes a decrease in the amount of creatine excreted. The author advocates the view that creatine is formed in relatively large quantities from a substance other than protein and that its utilisation is intimately connected with the metabolism of carbohydrate. H. W. B.

Vitamine Studies. I. The Catalase Activity of the Tissues in Avian Polyneuritis. R. ADAMS DUTCHER [with FERDINAND A. COLLATZ] (*J. Biol. Chem.*, 1918, **36**, 63—72).—The

catalase content of the tissues is lowered to the extent of 44% in avian polyneuritis. With the recovery from polyneuritis through the administration of vitamines (water-soluble *B*), there is a corresponding rise in the amount of catalase in the tissues until the normal figures are reached. Polyneuritis is accompanied, therefore, by incomplete oxidation, and consequently there is an accumulation of toxic products in the tissues. It is the function of the water-soluble vitamine to stimulate, directly or indirectly, the oxidative processes, and thereby effect the removal of these toxic compounds. In pigeon tissues, the content of catalase (as measured by the oxygen liberated from hydrogen peroxide), the metabolic activity and the content of water-soluble vitamine appear to stand in direct relation to one another. H. W. B.

Preparation of Antineuritic Substances from Carrots and Yeast. KANEMATSU SUGIURA (*J. Biol. Chem.*, 1918, **36**, 191—196).—Aqueous and alcoholic extracts of carrots and of yeast cure polyneuritis in pigeons. A colourless, crystalline substance capable of exerting a curative action on polyneuritic pigeons can be prepared from dried, powdered brewer's yeast by treating it with ten times its weight of 5% sodium chloride solution, and, after placing in a collodion bag, subjecting it to air dialysis (Kober, A., 1917, ii, 295). By this method, 22 mg. of colourless, crystalline substance, almost free from sodium chloride, can be obtained from 10 grams of dried yeast. A solution in water of from 2 to 5 mg. of these colourless crystals injected subcutaneously into a pigeon may be sufficient to abolish completely the symptoms of polyneuritis within a few hours. The crystals are not very soluble in water, and the solution gives a deep blue colour with Folin's phosphomolybdic–phosphotungstic reagent for the detection of phenolic substances. H. W. B.

Antiscorbutic Factor in Lemon Juice. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 259—269). —The free citric and other organic acids in lemon juice may be removed by precipitation with calcium carbonate without impairing the antiscorbutic power of the juice. If, after acidifying, the filtered lemon juice is evaporated in a vacuum at 30—40°, an active, dry residue is obtained which, when administered to guinea-pigs on an otherwise scorbutic diet, prevents the onset of scurvy. The treated lemon juice had a curative effect when given to a scorbutic monkey, but it did not seem to arrest the progress of well-marked scurvy in guinea-pigs when administered by subcutaneous injections. The administration of very concentrated doses of treated lemon juice previous to depriving guinea-pigs of the antiscorbutic factor does not prevent or delay the onset of scurvy. H. W. B.

Etiology of Scurvy in Guinea-pigs. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 270—274).— The fact that all the citrates can be removed from lemon juice

without impairing its antiscorbutic qualities (see preceding abstract) indicates that the antiscorbutic power of orange juice cannot be due to the laxative action of its constituent citrates, as contended by McCollum and Pitz (A., 1917, i, 604). Experiments are now described which prove that lactose and other carbohydrates do not possess the slightest antiscorbutic power, and the contrary results obtained by Pitz (*J. Biol. Chem.*, 1918, **33**, 471) are shown to be due to the considerable amounts of fresh milk (compare Chick, Hume, and Skelton, this vol., i, 360) instead of the carbohydrates in the diets employed by that worker. The authors draw the conclusion that scurvy in the guinea-pig does not arise through the absorption of toxins consequent to constipation in the intestine, but is due to the deficiency of a necessary accessory factor in the diet. H. W. B.

Genesis of Thiocyanic Acid in Animals. III. SERAFINO DEZANI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 189—207; from *Physiol. Abstr.*, 1918, **3**, 309. Compare this vol., i, 360).—After giving acetonitrile to dogs in toxic doses, hydrocyanic acid appeared in the urine. This transformation could not be brought about by organ (liver) infusions. Neither hydrocyanic nor thiocyanic acid was excreted after ingestion of purines and amino-acids.

H. W. B.

Pharmacology of the Hydroxyhydroaromatic Compounds. Y. SASAKI and K. OKUSHIMA (*Acta Schol. Med. Kyoto*, 1918, **2**, 257—270; from *Physiol. Abstr.*, 1918, **3**, 335. Compare Sasaki, A., 1917, i, 677).—The toxicity of these compounds towards frogs, as towards mammals (*loc. cit.*), diminishes as the number of hydroxyl radicles increases. When, however, the effects on separate organs are ascertained, some departures from the main generalisation are found. Paralysis of motor nerve-endings occurs only with *cyclo*hexanol and *i*-inositol. *cyclo*Hexanol exerts a paralysing action on muscle, whilst *i*-inositol shows first excitation and later paralysis. Phloroglucinol produces only excitatory effects on the heart; *i*-inositol causes slowing and irregularity of cardiac contractions, whilst *cyclo*hexanol causes weakening of systole.

H. W. B.

Pharmacology of the Vitamines. II. FR. UHLMANN (*Zeitsch. Biol.*, 1918, **68**, 457—498. Compare this vol., i, 419).—The action of vitamine preparations from various sources (orypan, extracts of oats, nettles, blood, etc.) on animal tissues is closely paralleled by the actions of pilocarpine and choline. The intestinal muscles are caused to contract, the action of the heart is depressed, the blood pressure is lowered, and the blood vessels dilated exactly as occurs when the respective tissues are treated with pilocarpine. Moreover, the action of the vitamine, like that of pilocarpine or choline, is antagonised by atropine. The conclusion previously drawn by the author is therefore confirmed,

namely, that the antineuritic vitamine is a substance physiologically closely related to pilocarpine, which acts on the sympathetic nerve-endings and thus exerts a controlling influence on the tonus of the muscles in the organism. H. W. B.

Agricultural Research Institute Library 1923 28 AUG 1924 Coimbatore

Chemistry of Vegetable Physiology and Agriculture.

Antiseptic Properties of certain Organic Compounds. I. J. KLIGLER (*Proc. Soc. Amer. Bacteriologists, Abstr. Bacteriol.*, 1918, **2**, 19; from *Physiol. Abstr.*, 1918, **3**, 350. Compare this vol., i, 469).—The composition and the degree of acidity of the medium exert a marked influence on the antiseptic properties of aniline and its derivatives. The higher the concentrations of organic nitrogenous compounds in the medium, the lower is the effective concentration of the antiseptic. H. W. B.

Theory and Practice of Disinfection by Alcohol. JOHANNE CHRISTIANSEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 275—305).—The disinfecting power of an alcohol depends not only on its ability to precipitate the proteins of bacteria, but on its capacity to penetrate the cell walls, and thus exert its action on the protoplasm of the bacteria. The latter quality is dependent on the surface tension of the alcohol. Propyl alcohol seems to be the most suitable of all the alcohols for direct application to the skin as a means of disinfection prior to surgical operation. Its toxicity is considerably greater than that of ethyl alcohol, and on account of its dissolving power over fats, it is able to enter readily the pores of the skin. H. W. B.

Yeast Growth. ARTHUR SLATOR (*Biochem. J.*, 1918, **12**, 248—258).—The author describes a method of measuring rates of growth of yeast cells by direct observation under the microscope.

When old yeast cells are introduced into a fresh medium, they remain quiescent for some time (lag). They then start growing at the normal unrestricted rate, and subsequent growth proceeds normally in alternate periods of rest and growth. Carbon dioxide retards growth. Air (oxygen) is essential for yeast growth; oxygen, chemically combined in the medium, as well as dissolved oxygen, may be utilised by the yeast. [See, further, *J. Soc. Chem. Ind.*, 746A.] H. W. B.

Agricultural College Library 1920 Coimbatore